ADVANCES IN NICKEL-BASED OLEFIN POLYMERIZATION CATALYSIS

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Polyolefins comprise the majority of the world's plastics consumption. Polyethylene and polypropylene are the two most widely utilized materials due to their exceptional properties and their inexpensive monomer feedstock. However, the polymers' true success derives from the heterogeneous catalysts that produce them. The discovery of these catalysts by Ziegler and Natta in the mid 20th century allowed for the linearity of polyethylene and the regio- and stereoregularity of polypropylene to be inherent in the microstructures. Additionally, the catalysts' simplicity and effectiveness are what make them the primary method for the commercial synthesis of polyolefins.

The homogenous analogues of the Ziegler-Natta catalysts have given researchers the opportunity to tailor the properties of the polyolefins even further. Early group metal catalysts have been prominently studied due to their similarity to the heterogeneous systems. However, the arrival of late-transition metal catalysis for olefin polymerization delivered the ability to control microstructures in new ways as well as tolerate functionality. This work describes the investigations into the development of new nickel-mediated processes for the polymerization of olefins.

Nickel (II) α-diimine catalysts have been previously developed for the regioregular ω-2 enchainment of α-olefins. However, controlling the tacticity has proven to be quite difficult. Chapter two describes work toward further controlling the stereoselectivity of these catalysts to produce ω-2 enchain poly(α-olefins) with high isotacticity, and in the case of 1-butene, a new class of semi-crystalline polyolefins.

Ligand sterics and electronics aid in the elucidating mechanistic insight into this unique polymerization.

Chapter three regards the development of an open geometry neutral nickel catalyst exhibiting high activity in ethylene polymerizations. The presence of bulky substituents on an amidinate ligand protects the axial sites of an active square-planar nickel center from associative displacement of a growing polymer chain, producing higher molecular weight polymer with greater activities than previously reported catalysts of this type. The addition of copper (II) bromide further enhances the activity of the catalyst by producing higher turnovers and achieving a much more narrow molecular weight distribution. Possible explanations for the copper's effect are discussed.

BIOGRAPHICAL SKETCH

Pasquale Iacono was born on September 19, 1984 in Brooklyn, New York to parents Maria and Joseph, both immigrants from Italy. After spending the first four years of his life in Brooklyn and two more in Houston, Texas, he spent the majority of his life in Endwell, New York, a suburb of the great city of Binghamton. It was while attending Homer Brink Elementary that Pasquale became interested in science, where he aspired to be a paleontologist. This was around the time Jurassic Park was hugely popular…not really any coincidence there. After fifth grade he continued his education at Maine-Endwell Middle School, where he started joining some of the offered honors classes and getting acclimated to no longer wearing sweat pants every day of his life. It was also in seventh grade where Pasquale was coerced into joining the modified football team, a hobby that would change his life forever.

Moving on the Maine-Endwell Senior High, Pasquale was enrolled in most honors classes, except for the science class (oddly). However, it was Mr Edward Lamoureux's chemistry class that he knew that he would go to college for chemistry. High school was quite the artistic time for Pasquale as well, where he part of the chorus, the madrigal choir, and the barbershop quartet. He continued to play football for the entire four-year span of high school (as well as track and field, but that was mainly to train for football), ultimately under the head coaching of the late Dick Russ. Senior year capped off Pasquale's public school career quite nicely, where he continued to be a captain of his football team, playing in the regional all-star senior game, and graduating seventh in his class. He also fine-tuned his pizza-making abilities, working in the kitchen of the local Chuck E. Cheese's for multiple years during and after high school.

Deciding by early decision and never even visiting the campus, Pasquale ventured to Ithaca College for his higher education. Under the advisement of professor Heinz

Koch, he knew chemistry was the way to go. After taking some vital classes including Professor Michael Haaf's general, organic, and advanced organic chemistry courses, as well as performing research in Prof. Koch's labs, he decided to embark to graduate school for organometallic chemistry. Pasquale continued to play football throughout his college years, but not for the school. In order to concentrate on his studies during the year, Pasquale played in the summers for semi-pro teams form the Binghamton area, one year for the Southern-Tier Green Machine and three years for the Broome County Dragons. This balance between football and school had still allowed Pasquale to achieve captain status after two years of playing and still graduating *magna cum laude* with honors.

Still staying close to home, Pasquale jumped to the other hill to join the graduate school at Cornell University, where he studied polymer synthesis and catalyst development under the advisement of Professor Geoffrey W. Coates. Numerous industrial and academic collaborations in such a rich and applicable field sold Pasquale as a chemist to continue on in research, even after a tough five years. He has therefore taken a post-doctoral position at Memorial Sloan Kettering Cancer Center in New York City under the advisement of Dr. Moritz Kircher after graduating in July 2012.

Dedicated to my loving parents, Maria and Joseph.

ACKNOWLEDGMENTS

This is the only part where I kind of get to say what I want, so I think I'm just going to spill my thoughts (there might be a few sentence fragments).

First and foremost, I thank my parents. They have supported me in all of my endeavors, no matter what, and have sacrificed in multiple ways so that I could be as happy and successful as possible. I also thank the rest of my family—my brothers Salvatore and Marcello, Aunt Nietta, Uncle Sean, Uncle Tonino, Cousin Rory and my grandmother, Gemma. My Uncle Pepino and my Aunt Enza will always be in our hearts, and this modest body of work is also dedicated to them. It's a small family, but we know how to take care of each other,

Of course, I wouldn't be here if it weren't for the teachers who have kept me learning and kept me wanting to learn. People like Mr. Kevin Wagstaff, Edward Lamoureux, Fitz Stewart, Regan Beers who have helped me think in different ways. Professors like Michael Haaf, Scott Ulrich, and Heinz Koch knew how to teach properly and instill general ideas at the higher levels. And at even higher levels, people like Prof. Paul Chirik and Prof. Bruce Ganem who really know how to explain tough concepts by simply using a chalkboard. In addition, all of these teachers were key influences in all of the major decisions I've had to make throughout my academic career.

This is where I would like to thank Geoff Coates. He knows how to do his job right. He stuck with me even through some tougher times and has even given me the freedom to explore some of my own ideas (see chapter 3). A great advisor, an even greater person. I guess along with this I should thank the funding sources that came along with working for him, including Mitsubishi Chemical and the Cornell Center for Materials Research. Collaborators such as Ed Kramer (University of California Santa Barabra), Fanny Deplace, (UCSB) Rufina Alamo (Florida State University) and

Carolina Ruiz-Orta (FSU) have been great people to work with from a distance as well, and have always provided great results for us. Special thanks to Ivan Keresztes for doing a lot of great analysis on some tough compounds, and Emil Lobkovsky for being able to get crystal structures from substances that I didn't even think were crystals.

There are way too many friends that have influenced me in some way or another. I'll try my hardest. Start with really old friends. Adam Sterling has always been there. He really taught me how to look at life from a different perspective. A great companion. Matthew Scudder and Matthew Barcak, although I don't get to see them much anymore, have been great people to grow up with. It's these people who mold you early on in life. Steve Potochniak is a great guy. I'm also thanking, in no particular order, Dan Cordaro, Mike Salvagio, Mike Sills, Charlie Messenger, Lee Sacks, and Scott Lipowitz for being fantastic college buddies.

Heather Donahoe will always hold a special place in my heart for all that her and her family have done for me.

Graduate School has brought me some fantastic people who are right up there with my old high school friends. Henry Kostalik, Kevin Noonan, Tim Clark, Syud Ahmed, and Bryan Whiting are men amongst boys. Unnecessary to put stories in here. We know what's up. In addition to these fellows, there are people who have helped me mature as a chemist in addition to those five guys. Most importantly, Brian Long. I love him. Broke my heart to tell him I wasn't working for him after grad school. We will start that BBQ team though. I'm also thanking Nick Robertson for being a good person talk to during some rougher times. Giang Vo has been a good partner as the polyolefin subgroup started to dwindle in numbers, and he helped keep it strong. Connections with guys like him, as well as Chad Ellis, Soumya Sarkar, Michael Mulzer, and Hisashi Ohtaki are priceless. Its also been great with the various people

I've worked with in the group, including Rachna, Tam, Yuki, and Angie, all of which were always interested in what I had to say, scientifically or not. They are all very bright, and I wish them luck along with the other young folks in our group.

Football has been a saving grace for me, and there are plenty of guys that I would like to thank here. Coach Angelo for throwing me in at nose guard to "give it a shot"—what ensued changed my life. Coach Beers, Coach Russ (God rest his soul) and Coach Touhey for looking to me as a captain and a good role model. I thank Coach Jud Blanchard, Tom Manny, and Cleon Myles as coaches who saw my potential in the minor league circuit. Players such as Willie Everett and Bobby McKnight are people that you "fight in the trenches" with, and it's the connection with guys like these that are cherished forever. As a captain, I would like to thank those ten other guys I look at in the huddle before every play, no matter who they are.

A couple of random things: Metallica, Megadeth, eggs, Hall and Oates, Samsung, Microsoft, Sony, Little River Band, The Guess Who, Jack Black, Dethklok, Disturbed, System of a Down, Iced Earth, Red Hot Chili Peppers (and our tribute band), coffee, Hal's, the Hilton, TCAT, the New York Football Giants, Gianluigi Buffon, Uncle Joe's, the Westy, my porch, lentils, my Jeep, boots, and the 4-4 defense.

I would finally like to thank Jenna Santucci for helping me through my last year of grad school. One of the nicest and sweetest people I've ever met. She helped me get back to eating healthy and to reappreciate a few finer things in life, like my wonderful dog Heineken.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF SCHEMES

LIST OF TABLES

CHAPTER ONE

Polyolefin Architectures Synthesized From Late Transition Metal-Catalyzed Chain-Walking Polymerization

1.1 Introduction

The original syntheses of polyethylene (PE) and polypropylene (PP) by Ziegler-Natta catalysts required simple heterogeneous precursors that produced highly regio- and stereoregular polymers.[1] The heterogeneous compounds, usually magnesium supported titanium (III) chloride, now yield the most widely consumed synthetic materials worldwide.[2, 3] The production of polyolefins for years to come will likely depend on the use of these catalysts. However, alternative methods to enable control of tacticity and molecular weight as well as achieving new microstructures are desired, as these properties are more difficult to tune with ill-defined heterogeneous catalysts. The advent of homogeneous catalysis enabled variables such as ligand structure, metals, solvents, and coinitiators in metallocene[4] and nonmetallocene-derived[5] systems to be altered so we can attain the polymer properties we desire. For instance, the tacticity of a polymer and how a stereoselective catalyst can dictate the coordination and insertion of a prochiral monomer has been extensively studied and reviewed.[6] Not only are there new ways to achieve isotactic polymers homogeneously, but pathways to syndio- and hemitactic polymers are now available. Homogeneous catalyst development has allowed for the incorporation of polar functionality,[7] and achieving living behaviors with vinyl-insertion polymerization catalysts can provide precisely sized polymers with narrow molecular weight distribution for the ultimate goal of the syntheses of block copolymers.[8]

The synthesis of new polyolefin materials has also depended on the exploitation of fundamental organometallic transformations. For instance, the controlled transmetallation of a growing polymeryl to a main-group metal can result in multiple

polymer chains to be synthesized with precise molecular weights[9] and end group functionality.[10] Zinc-based reagents can shuttle growing chains between two active metal-centers with different catalytic behaviors, allowing for the development of polymers with blocky-type microstructures.[11]

β-X elimination of a polymer from a metal is an alternative route to novel microstructures. β-Halide elimination results in polyolefins with unsaturated end groups, in addition to yielding multiple chains per metal.[12] Vinyl halides or alkoxides are most commonly employed for this purpose, where insertion of a functionalized olefin will lead to β-X elimination followed by reintiation of the active species by an alkyl aluminum. Controlling the end-functionalization of a growing chain can also yield polymerizable allyl groups, and therefore, macromonomers can be acquired. Polyolefin macromonomers can be subsequently copolymerized with olefins to yield materials with various properties, from compatibilized materials[12c,13] to thermoplastic elastomers.[14]

β-H elimination is also well established as a route to macromonomers[13b,c,13g,15] as well as a general termination pathway in group IV catalyzed olefin polymerizations. The elimination of a hydride instead of an alkoxide or halide is a more attractive route to end-functionalization and multi-chain production, mainly due to the absence of expensive and occasionally toxic chain-transfer agents. However, β-H elimination has proven to be quite useful in olefin polymerizations catalyzed by late transition metals, mainly nickel and palladium. This lead to a relatively unexplored phenomenon known

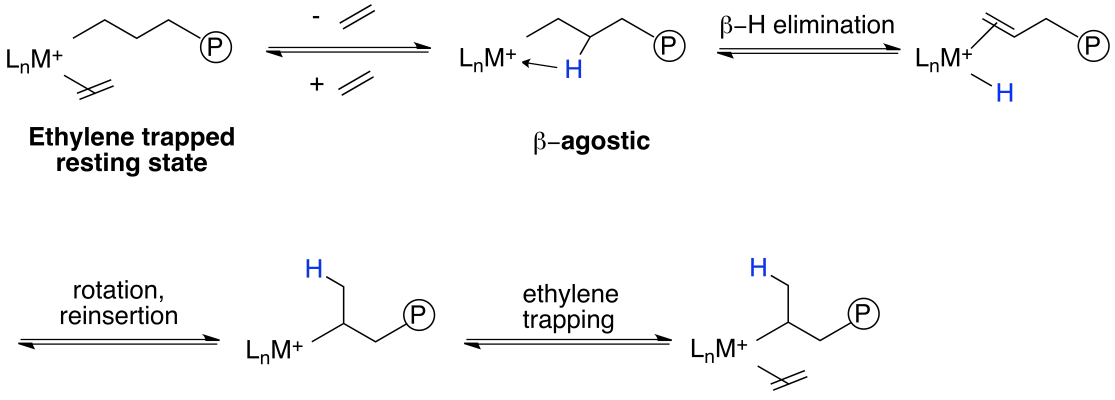
as chain-walking polymerization. This review will focus on the developments of new architectures derived from this mechanistically unique process.

1.2 Brief Overview of Chain-Walking

In the late 1980's, Fink and Möhring synthesized low molecular weight, branched polyethylene using an iminophosphonamide nickel complex.[16] The authors claim that the nickel undergoes a "migration" along the polymer chain to produce primarily methyl branches. This study expanded on the Shell higher olefin process (SHOP) utilizing nickel-based catalysts that make linear short chain α-olefins. Formation of short chain oligomers were attributed to the facile associative displacement of an appended alkene from the cationic metal hydride.[17] Higher pressures and temperatures ultimately allow propagation to proceed at a faster rate than termination.[18]

The cationic nickel and palladium complexes for the polymerization of ethylene and α-olefins discovered by Brookhart and coworkers suppress associative displacement of the appended unsaturated polymeryl.[19] The occupation of the area near the axial sites of the square-planar active metal center by bulky substituents on the N-aryl moieties blocks oncoming olefins and other chain transfer reagents such as aluminum alkyls. This gives an appended long-chain alkene the freedom to rotate about its coordination bond with the metal center and reinsert to form a methyl branch. Repetition of sequential β-H eliminations, rotations, and reinsertions can result in longer branch lengths. This aptly-named chain-walking process, in concert with periodic coordination and insertion of olefinic monomers, gives rise to a chain-walking polymerization.

Mechanistic studies of the chain-walking mechanism for both nickel and palladium mediated polymerizations have been reported by Brookhart and coworkers.[20, 21] The authors sought to observe various metal-alkyl complexes at low temperatures and measure their rates of β-H eliminations and insertions of ethylene. As predicted, the chain isomerization event is initiated by the displacement of ethylene from the resting cationic state to form a β-agostic species (Scheme 1.1). An energetically low β-H elimination, followed by olefin rotation and reinsertion forms the secondary metal-alkyl species. For palladium complexes, β-H elimination occurs at a lower energy barrier than that of the nickel complexes (≈7 kcal/mol versus ≈14 kcal/mol). In addition, ethylene insertion into a metal-alkyl bond is approximately 4-5 kcal/mol lower for nickel versus palladium. These results help explain the decreased branching contents of polymers produced by nickel catalysts and rationalize the use of palladium complexes for the synthesis of hyperbranched polyethylene (*vide infra*).



Scheme 1.1 Mechanism of chain-walking process in the synthesis of branched polyethylene.

The effects of ligand substituents and polymerization conditions on the chain-walking process have also been investigated. Adding electron-withdrawing groups to a ligand framework encourages agostic interactions; therefore β-H eliminations occur more readily to produce a higher branching content.[22] Conversely, electron-donating ligands inhibit these processes and thus encourage ethylene insertion over chain-walking. Increasing the bulk on the ortho positions of the N-aryl groups has been shown to increase branching contents. It has been suggested by Gates *et al*. that these larger groups shield the alkyl cation more readily from ethylene, allowing for a more facile agostic interaction and subsequent hydride elimination.[23] The authors also conducted a thorough study on the effect of ethylene pressures and temperatures and show an increase in branching behavior at higher temperatures and low pressures, presumably due to inhibited binding of ethylene, which encourages the unimolecular β-H elimination event.

1.3 Ethylene Based Polymers

Understanding the mechanism of late-transition metal-mediated olefin polymerizations and their chain-walking pathways has led to a surge in development of nickel and palladium complexes to control these processes.[24] The first major impact of these polymerizations was in the synthesis of branched polyethylene. The ability to use a single monomer feedstock and control the branching contents of the material it produces at moderate temperatures and pressures is highly attractive. This method rivals the commercial free-radical-based processes to produce low-density polyethylene (LDPE) and linear low-density polyethylene (LLDPE), which usually

require α-olefin comonomers in addition to high temperatures and pressures. DuPont has trademarked some of these catalyst systems under the name Versipol, although currently no plants have been instituted for commercialization.

The ability to control the topology of polyethylene and ultimately produce hyperbranched polyethylene (HBPE) was pioneered by Guan and coworkers. The authors utilized α-diimine palladium catalysts and low ethylene pressures to allow for extensive chain-walking processes to occur. The polymers produced exhibited molecular weights > 150 kDa and narrow molecular weight distributions, indicative of the single-site catalysis that achieved them.[25] The intrinsic viscosity of the PE produced at low pressures of ethylene (10 kPa) was an order of magnitude less than that of atactic polypropylene (aPP) with similar molecular weights. The intrinsic viscosity, in addition to the sub-unity ratios of the radius of gyration to the hydrodynamic radius,[26] was indicative of the dendritic nature of these hyperbranched architectures.

The initial work by Guan *et al*. had generated numerous investigations into the synthesis of modified HBPEs and the properties[27] of such polymers. Although there are multiple reviews of this area in the literature,[28] it is worth noting some of the more interesting microstructures produced utilizing HBPE and its synthetic methods (Figure 1.1). Copolymerization with functional monomers such as acrylates in a chain-walking mechanism can yield highly branched-polyethylenes with end-functionalized branches.[28c] Incorporation of functionalized macromonomers can result in core-shell-type nanostructures, and insertion of a diene or a cyclic comonomer can produce breaks in a polymerization to produce a "necklace" of HBPE dendrons.[28a]

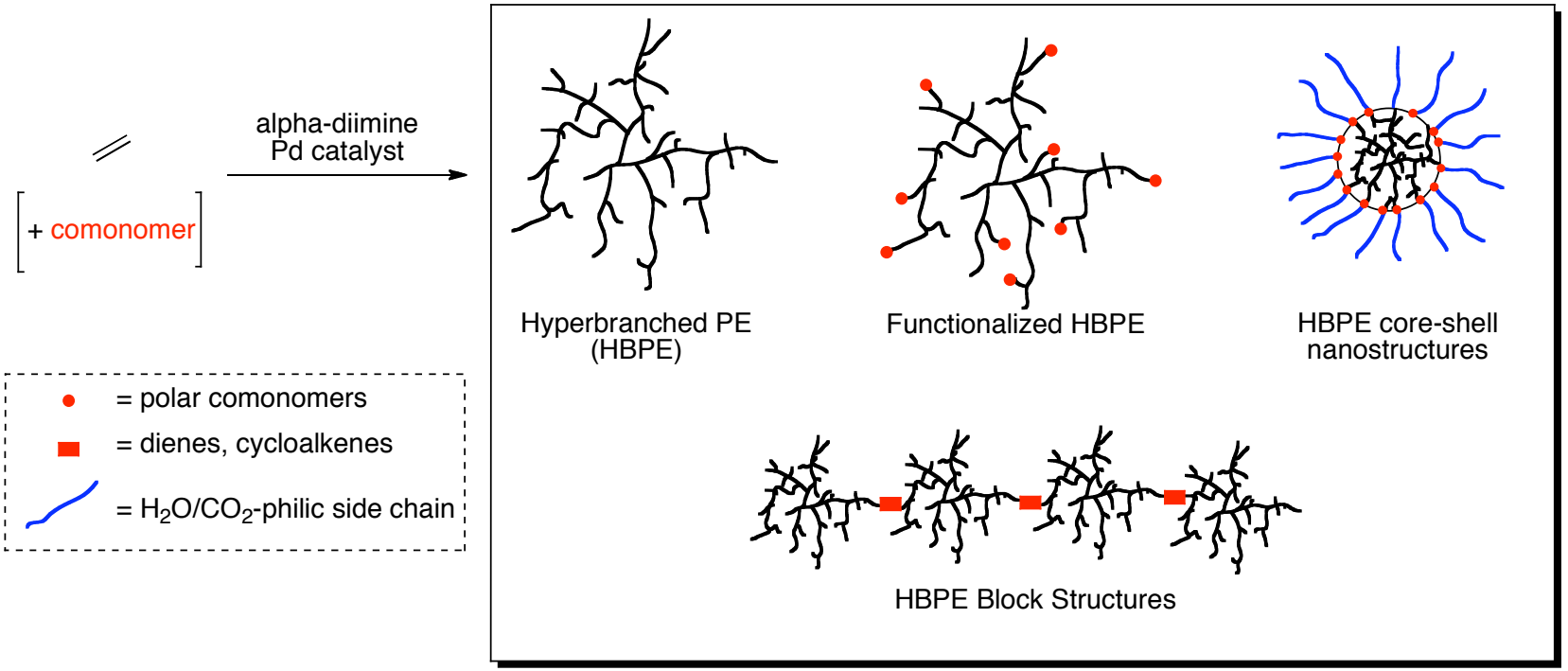


Figure 1.1 Various hyperbranched polyethylene structures produced using chain-walking catalysis.

Sun *et al*. synthesized these polymers via a more controlled approach. The polyethylene dendrimers were polymerized from palladium catalysts that were periodically appended on a polynorbornene backbone, synthesized by ring-opening metathesis polymerization (ROMP).[29] The structure of these polymers was confirmed by size-exclusion chromatography (SEC), NMR, dynamic light scattering (DLS), and AFM imaging (Figure 1.2). Similarly, blocky structures of HBPE and linear PE have been produced using either a living[30] or a chain shuttling approach.[11a]

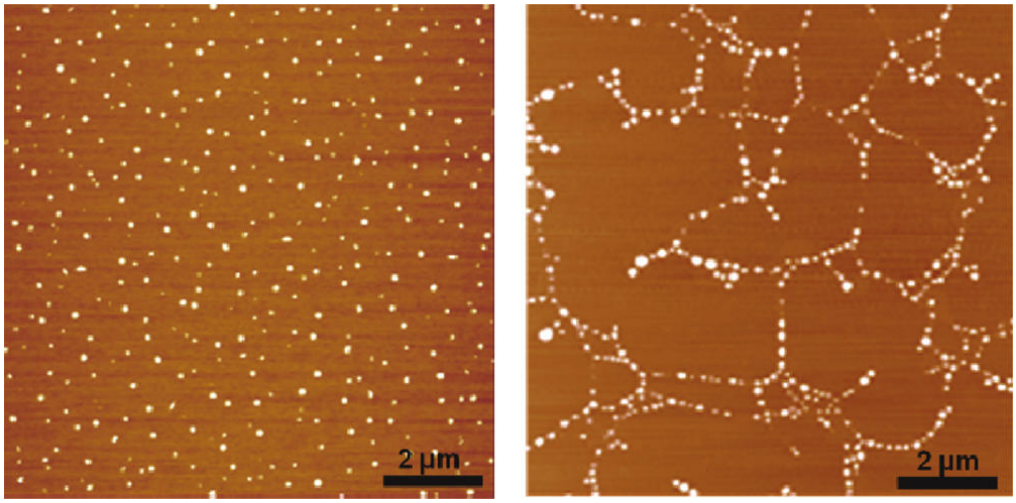


Figure 2.2 AFM images of hyperbranched polyethylene (HBPE) dendrimers (left) and "necklace" polymers which HBPE "beads" (right). Reproduced from *ref* 29.

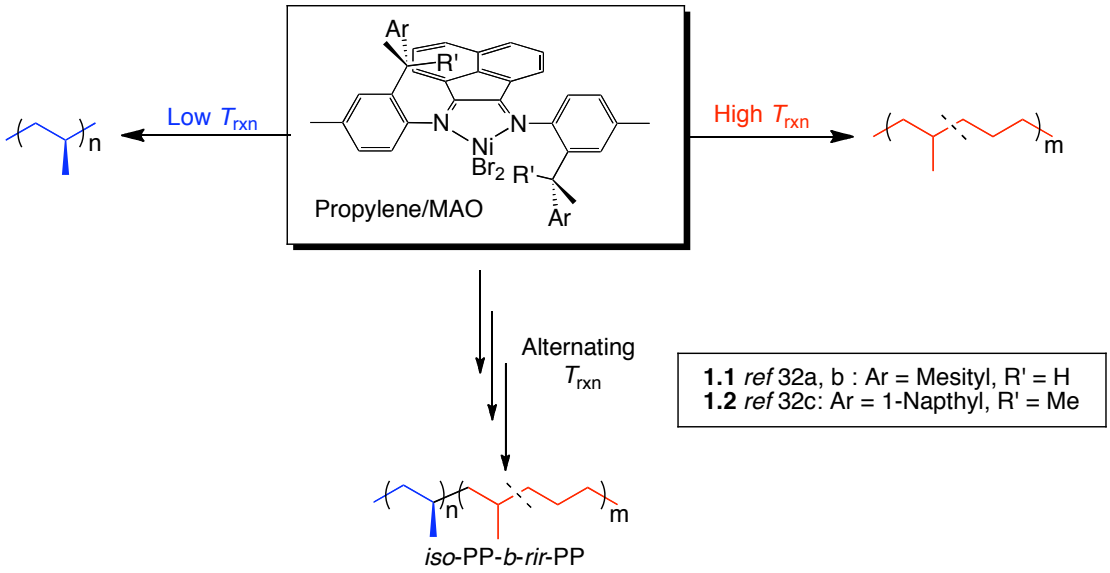
1.4 Non-Functionalized Olefin-Based Polymers

1.4.1 Terminal Olefins

1.4.1.1 Propylene

A major highlight of the original Brookhart catalysts was their ability to polymerize α-olefins other than ethylene. The polymers produced were amorphous, exhibiting low glass transition temperatures (T_g), and the authors acknowledge chain-isomerization events to produce regioirregular PP (rirPP).[19a] The formation of rirPP was attributed to propylene units that insert in a 2,1 fashion.[19b] The metal can then walk to the methyl group of the inserted propylene and form a 3,1-insertion unit (Scheme 1.3).

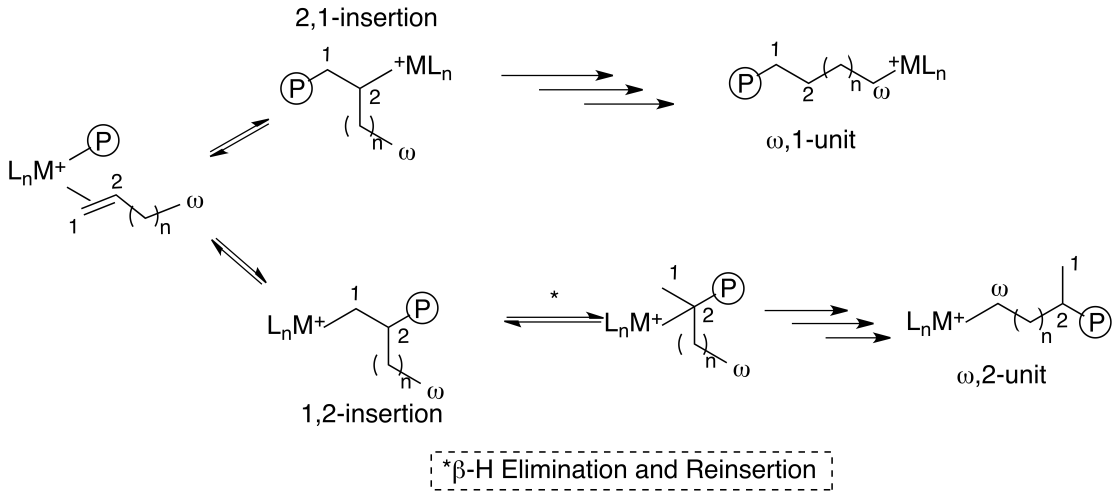
A more controlled polymerization of propylene utilizing late-transition metals can occur at lower temperatures. The polymerization of propylene by C_s- and C_1-symmetric α-diimine nickel (II) catalysts at lower temperatures decreases the chain-isomerization events, producing a syndiotactic polypropylene (sPP) dictated by a chain-end control mechanism.[31] Coates and coworkers have reported C_2-symmetric α-diimine nickel (II) catalysts for the isoselective polymerization of propylene at low temperatures. Because these catalysts also exhibited living behaviors, block copolymers could be synthesized, where blocks produced at low temperatures gave semicrystalline iPP and at high temperature rirPP (Scheme 1.2). The iPP blocks can crystallize and anchor the amorphous segments, inducing a microphase separation and affording thermoplastic elastomers.[32]



Scheme 1.2 Synthesis of regioblock copolymers of propylene using living nickel (II) catalysts.

1.4.1.2 Higher Terminal Olefins

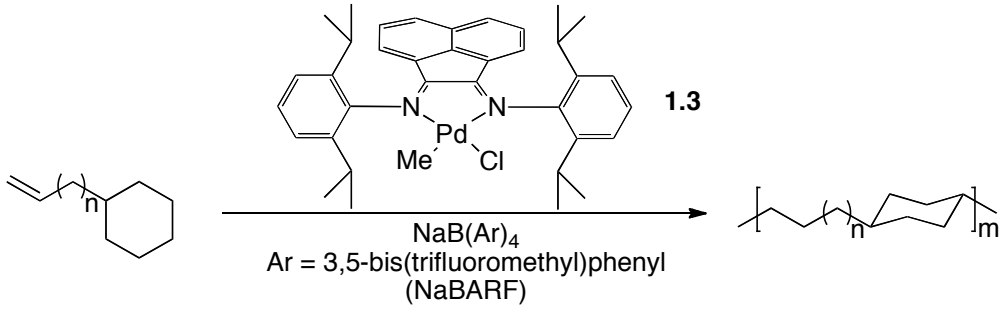
The chain-walking polymerization of α-olefins larger than propylene can result in more complex microstructures. Scheme 1.3 depicts the two major pathways of an α-olefin as it is enchained into a metal-alkyl species. A 2,1-inserted olefin can allow for the metal to chain-walk to the ω-position, producing an ω,1-inserted unit. Conversely, a 1,2-inserted monomer will encourage chain-walking to produce an ω-2 unit. However, monomer insertion into a secondary metal-alkyl is possible, as well as sequential insertions without β-H elimination. Chain-walking can occur at any intermediate along these pathways and can afford a polymer with branches longer than methyl.



Scheme 1.3 Major pathways for enchainments of α-olefins in a chain-walking polymerization.

Although there are numerous reports of the synthesis and characterization[33] of the complex chain-walked architectures derived from higher α-olefins, mainly 1-hexene[34] and 4-methyl-1-pentene,[35] controlled polymerizations have been demonstrated to produce chain-straightened poly(α-olefins) with very high regioselectivities. For instance, the chain-straightening polymerization of 1-octadecene will give a microstructure similar to linear polyethylene with a few methyl branches. This polymer exhibits a melting transition, and has been introduced into living polymerizations as a "hard" block for the synthesis of thermoplastic elastomers.[19b] Coates and coworkers have also reported the highly selective ω-2-enchainment polymerization of various α-olefins.[36] These ethylene-propylene (EP) copolymer mimics have shown unique rheological behaviors,[37] and can thus be utilized in applications such as oil-viscosity modification.

The regioselective enchainment polymerization of alkene-substituted cyclohexanes has also been regioselectivity demonstrated by Takeuchi (Scheme 1.4). These polymerizations incorporate a cyclic unit within a polyolefin structure, which can have influences on its thermal and mechanical properties as well as its chemical stabilities and optical transparencies (see Section 1.4.2.2).[38] The author reports melting transitions (T_m) up to 226 °C, with decreasing T_ms as the carbon spacer between incorporated cyclohexanes increases in length.



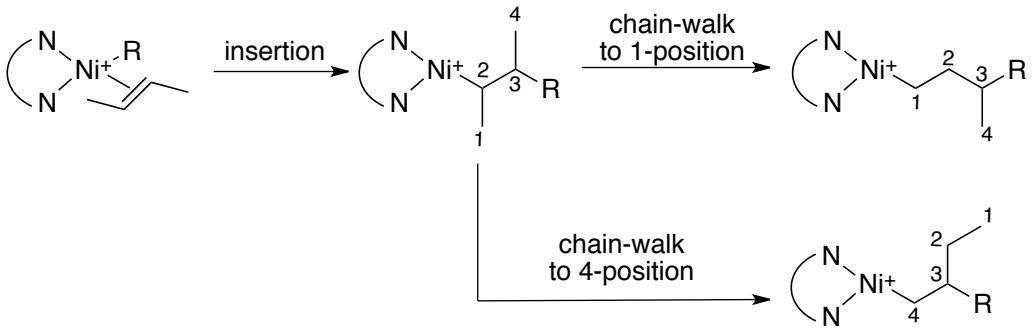
Scheme 1.4 Synthesis of cyclohexane enchained polymers by the polymerization of alkenylcyclohexanes.

1.4.2 Internal Olefins

1.4.2.1 2-Butenes

The late-metal catalyzed polymerization of internal olefins can allow for a more regioregular architecture due to more sterically dictated chain-walking pathways. Scheme 1.4 depicts the enchainment pathways of *trans*-2-butene.[39] After insertion of the monomer, it can either walk to the 4-position to produce a β-ethyl branch or walk to the 1-postion to produce a γ-methyl branch. The smaller and more distant branch

will be energetically favorable for subsequent coordination and insertion of the next monomer.



Scheme 1.5 Insertion pathways for *trans*-2-butene in nickel (II)-catalyzed polymerizations.

The polymerization of *trans*-2-butene was first reported by Leatherman and Brookhart in 2001, and marked a milestone in the polymerization of acyclic internal olefins.[39a] Not only was it the first reported polymerization of *trans*-2-butene, but it was also highly regioselective, incorporating <10% ethyl branches. In a polymerization involving an isomeric mixture, Milano *et al*. reported that similar coordination energies of the *cis*- and *trans*-butenes do not hinder propagation of the more reactive *E* isomer.[39d]

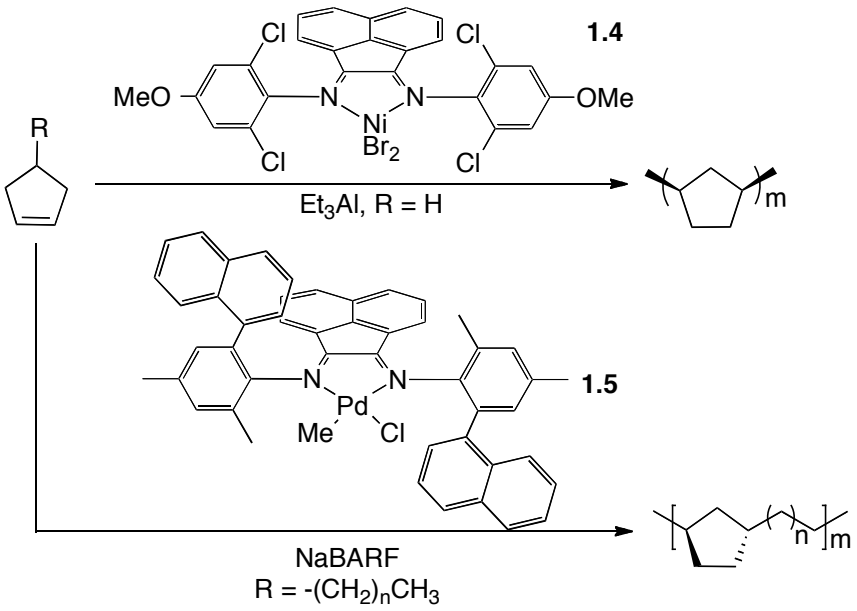
Cherian *et al*. reported the isoselective and regioselective enchainment of *trans*-2-butene using a C_2-symmetric α-diimine nickel (II) catalyst.[39b] The monomer inserts via an enantiomorphic site control mechanism, producing [*mm*] triads up to 0.64 and exhibiting melting transitions up to 66 °C. This was the first report of a late-transition

metal-mediated chain-walking polymerization that was dictated by chiral ligand environment.

1.4.2.2 Cycloalkenes

Cyclopentene vinyl-insertion polymerizations were originally developed using early-metal Ziegler-Natta catalysts in the early 1990s.[40] Using C_2-symmetric metallocenes, *cis*-isotactic 3,1-inserted poly(cyclopentene) was achieved, albeit to low molecular weights. It was not until 1998 when Brookhart reported polymers synthesized to high molecular weights using late-transition metals.[41] He reports that the 1,2-inserted unit cannot be observed at low temperatures and presumably rearranges immediately to the 3,1-inserted β-agostic species. The fact that nickel and palladium can chain-isomerize without displacement of an appended alkene better than early-metal catalysts can explain the differences in molecular weights.

The polymers produced by Brookhart had moderate tacticities ([*mm*] = 0.66), but Takeuchi and Osakada reported a highly *trans*-isoselective and regioselective enchainment of 4-alkylsubstituted cyclopentenes using a C_2-symmetric α-diimine palladium (II) catalyst (Scheme 1.5).[42] With a methyl substituent, the authors report an [*mm*] > 93%. With longer substituents, the polymers' tacticities cannot be elucidated from NMR measurements. However, the crystallinity can be observed by X-Ray diffraction measurements, which indicated their isotactic nature. The polymers were also observed to exhibit liquid crystalline behavior by polarizing optical microscopy.



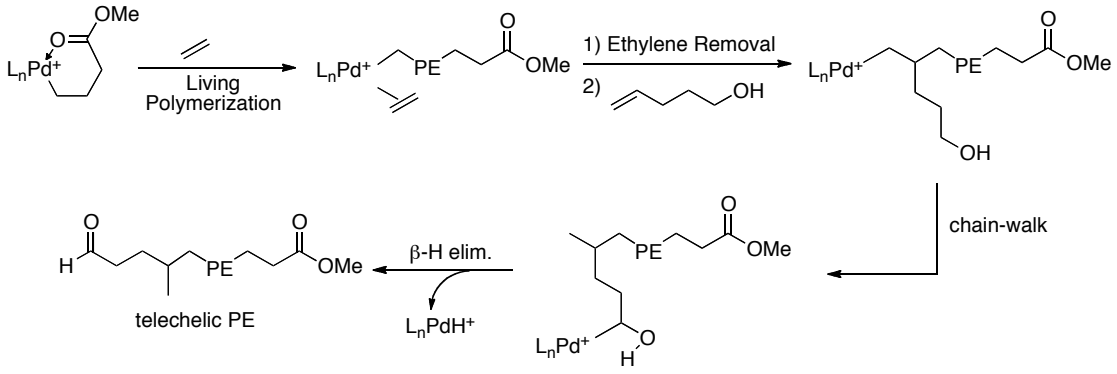
Scheme 1.6 Synthesis of poly(cyclopentenes) by chain-walking polymerization.

1.5 Functionalized Olefin-Based Polymers

The incorporation of functionalized α-olefins into late metal-catalyzed polymerizations has been reported.[7] However, monomers such as (meth)acrylates and vinyl halides/ethers/acetates contain functionality on the β-position and therefore do not β-H eliminate to undergo a chain-walking event. A stable chelate usually hinders this process, which is why most functional comonomers must be copolymerized with ethylene to achieve any incorporation.

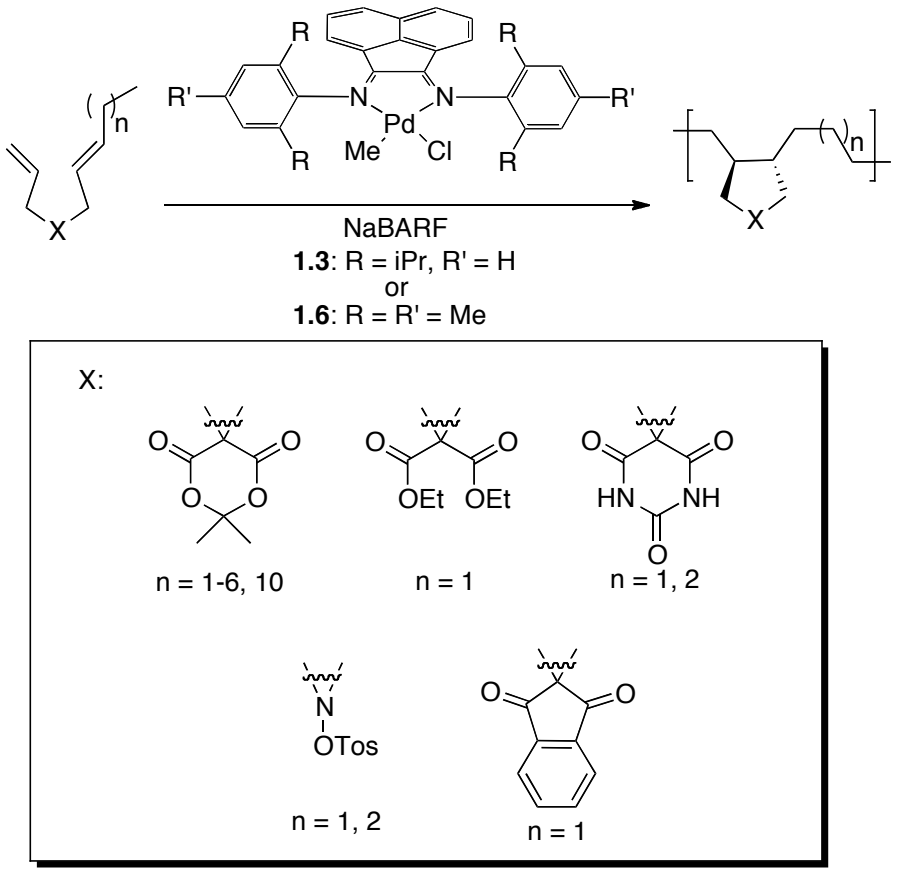
Limited work has been done on the chain-walking polymerization of functionalized long-chain alkenes. Gottfried and Brookhart have utilized 4-penten-1-ol as a chain-transfer agent to make telechelic polyolefins (Scheme 1.6).[43] Using a living palladium-acrylate chelated catalyst, ethylene is inserted to form ester terminated PE.

After removal of the ethylene monomer, the functionalized alkene is introduced. The metal can chain-walk to the 5-position and β-H eliminate to form the aldehyde. Despite the fact that only one monomer is inserted and chain-walked, it provides an insightful route to polyethylene which is functionalized at both ends.



Scheme 1.7 Synthesis of telechelic polyethylene by termination with a chain-walked comonomer.

Osakada and coworkers have reported the chain-walked cyclopolymerizations of functionalized monoterminal dienes (Scheme 1.7). After insertion of the terminal alkene, insertion of the internal alkene allows for chain-walking to the methyl, similar to the 4-alkyl-substituted cyclopentenes (see Section 1.4.2.2), allowing for a chain-straightened functionalized repeating unit. Some of the polymers formed were also moderately isotactic, exhibiting [*m*] diads up to 55%. Although they did not display any crystalline behavior, they do show a range of glass transition temperatures (15-195 °C) depending on the functionality.



Scheme 1.8 Synthesis of functionalized cyclopentene incorporated polyolefins via cyclopolymerization of monoterminal functionalized dienes

1.6 Outlook and Summary

Polyolefin architectures used to be limited by monomer reactivity and catalyst selection, but the development of chain-walking polymerizations by Brookhart and coworkers has opened a new gateway to novel materials with interesting properties. Monomers can be isomerized and manipulated in new ways by employing late-transition metal catalysts, allowing for a diverse array of microstructures. Highly branched structures can be synthesized from single monomers under mild conditions,

and regio- and/or stereoregularity can be instilled into the polymer, which result in materials with new thermal and mechanical properties. The development of new catalysts and monomers for such a unique process will be sure to provide the polymer community with exciting new results in years to come.

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CHAPTER TWO

Isotactic 4,2-Enchained Poly(1-butene) via C_2-Symmetric Ni(II)-! -Diimine Catalyzed Chain-Walking Polymerization

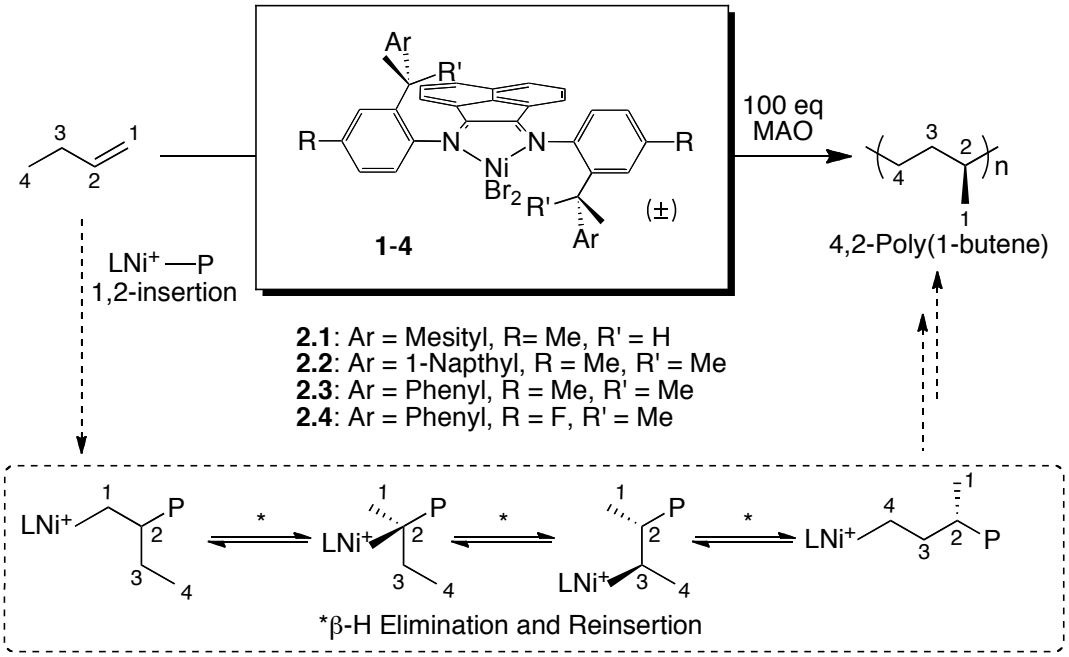
2.1 Introduction

The advent of late transition metal mediated olefin polymerization has enabled access to new polymer architectures. The decreased oxophilicity of late metal catalysts relative to traditional early metal catalysts has prompted considerable interest in the incorporation of various polar monomers. Additionally, late-metal catalysts undergo β-hydrogen elimination from the growing polymer chain without associative displacement, facilitating chain-walking polymerization.[1] For example, hyper-branched and dendritic polyethylene architectures with various topologies can be prepared through simple variation of reaction conditions without adding a second monomer.[2] These polymers exhibit properties similar to low-density polyethylene (LDPE), which are traditionally produced by free-radical processes that require high temperatures and pressures. We recently reported the synthesis of methyl-substituted polyethylenes from higher α-olefins using a nickel α-diimine/methylaluminoxane (MAO) catalyst.[3] This polymerization proceeds through an ω,2-enchainment mechanism (Scheme 1.3), yielding amorphous polymers with little to no crystallinity. The ability to control tacticity in a chain-walking polymerization mechanism would enhance crystallinity and remains a challenge in the field.[4]

Previously, we reported the partially isoselective enchainment of *trans*-2-butene to produce *iso*-4,2-poly(1-butene);[5] however, the resulting polymer exhibited low melting transition temperatures. Preliminary experiments utilizing the less expensive 1-butene to prepare *iso*-4,2-poly(1-butene) through chain-walking polymerization have shown increased isotacticity and melting transitions.[6] Additional motivation for use of this monomer arises from the recently increased production of 1-butanol, a

feedstock for 1-butene and a viable biofuel.[7] It would be advantageous to develop routes towards polyolefins using biorenewable feedstocks over petroleum sources.

Isotactic poly(1-butene) (PB-1) exhibits increased corrosion and impact resistance relative to isotactic polypropylene and poly(4-methyl-1-pentene), and the material is primarily employed in pipe and packaging manufacturing. However, its processability is restricted by a kinetically favored polymorph transformation at room temperature, which can negatively affect material densities in a molded setting. This limitation has been overcome recently, allowing PB-1 to be processed more feasibly.[8] Because of the commercial utility of PB-1, producing its isomeric form is of interest, potentially allowing useful polymers with different microstructures to be produced from the same bio-based feedstock. We recently reported cumyl-substituted α-diimine Ni(II) catalyst systems that produce polypropylene with improved tacticity and regiochemistry relative to the polymer produced with the analogous mesityl-bearing catalyst, **2.1**.[9,10] Thus, we expected the cumyl-based catalysts to afford good regio- and stereocontrol in 1-butene polymerizations. Herein we report the isoselective and regioregular ω,2-enchainment of 1-butene and 1-pentene using C_2-symmetric nickel catalysts containing cumyl-substituted diimine ligands (Scheme 2.1).

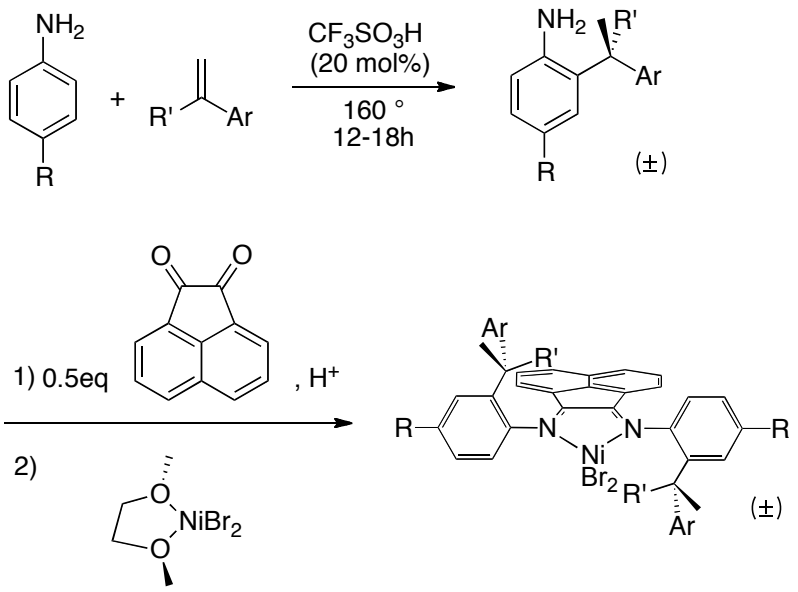


Scheme 2.1 Synthesis of isotactic 4,2 enchained poly(1-butene).

2.2 Results and Discussion

2.2.1 Synthesis of Catalysts

Catalysts **2.1**-**2.3** have been previously reported,[9] and catalyst **2.4** was synthesized in a similar manner, as generally portrayed in Scheme 2.2. A triflic acid-catalyzed *ortho*- alkylation of *para*-toluidine by the appropriate styrene yields the bulky aniline in moderate yields. The aniline is then condensed onto acenapthenequinone via an acid catalyzed imine condensation. Metallation onto (dimethoxyethane)$NiBr_2$ yields the α-diimine nickel complex in good yields as a dark red solid.



Scheme 2.2 General synthesis of chiral α–diimine nickel (II) bromide complexes.

2.2.2 Screening of Catalyst Conditions

We originally sought to determine the optimal catalyst conditions using 1-pentene, as it is a liquid monomer and thus easier to purify and handle (Table 2.1). Because we knew tacticity was a function of catalyst, we aimed to screen conditions that would provide us with polymers with the highest ω-2 regioselectivity. The lower temperatures predictably control the polymerization where 5,1-insertions are reduced to a minimum (Table 2.1, entries 6-11). These are due to initial 2,1 insertions, which will be less favorable at a lower temperature. The temperatures do not affect longer branch content, however, which is a result of subsequent insertions before incomplete chain-straightening. The addition of methylene chloride to the reaction afforded polymer with optimal 5,2-insertions with a minimization of 5,1-insertions and propyl/ethyl branches (Table 2.1, entry 11). A polar solvent may have influences on

the ion-pairing of the catalyst system, where a more vacant metal center can encourage 1,2-insertion as well the β-agostics to induce chain-walking (see section 1.2).

The other major influence was the cocatalyst used. Polymeric methylaluminoxane (PMAO) was the clear choice of alkylaluminum initiator, as the modified MAO (MMAO) provided much lower 5,2-enchained units (Table 2.1, entry 5). Diethylaluminum chloride did not make a substantial difference in the polymerization (Table 2.1, entry 6).

Table 2.1 Screening for 1-pentene polymerizations using **2.4**.[a]

entry	solvent	[pentene] (M)	cocatalyst	T_{rxn} (°C)	t_{rxn} (h)	yield (mg)	TOF[b] (h^{-1})	enchainment type (mole fraction)[c] 5,1	5,2	1,2	C_2 branch
1	PhMe	5.4	PMAO-IP	0	3.5	539	220	0.12	0.70	0.11	0.07[e]
2	neat	7.6	PMAO-IP	0	1.5	336	319	0.09	0.77	0.08	0.06[e]
3	PhMe	5.4	PMAO-IP	-20	24	480	29	0.03	0.85	0.09	0.03
4	neat	7.6	PMAO-IP	-20	17	334	28	0.02	0.85	0.10	0.03
5	neat	7.3	MMAO-7	-40	48	114	3	0.00	0.66	0.24	0.10[e]
6	neat	7.3	Et_2AlCl	-40	48	302	9	0.01	0.85	0.11	0.03
7	neat	7.6	PMAO-IP	-40	24	215	13	0.01	0.80	0.13	0.06
8	PhMe	5.4	PMAO-IP	-40	48	230	7	0.01	0.87	0.09	0.04
9	PhMe/Cy[d]	5.4	PMAO-IP	-40	48	107	3	0.01	0.83	0.10	0.06
10	PhCl	5.4	PMAO-IP	-40	48	389	12	0.00	0.88	0.11	0.02
11	CH_2Cl_2	5.4	PMAO-IP	-40	48	224	7	0.00	0.90	0.06	0.03

[a]10mL of 1-pentene, 5mL solvent, 10μmol of Ni complex (added as a solution in 2mL CH_2Cl_2), [Al]/[Ni]=100. [b]Turnover frequency (TOF)= mol 1-pentene/(mol Ni·h). [c]Determined using ^{13}CNMR spectroscopy. [d]2.4mL toluene, 2.6mL cyclohexane. [e]Also includes branching greater than three carbons.

Table 2.2 Polymerization of 1-butene and 1-pentene using chiral α–diimine nickel (II) bromide complexes.[a]

entry	monomer	complex	yield (mg)	M_n (kg/mol)[b]	M_w/M_n[b]	enchainment type (mole fraction)			[*mm*][d]	α[e]	T_m[f] (°C)
						ω, 1[c]	ω, 2[d]	1, 2[d]			
1[g]	1-butene	**2.1**	380	66.1	1.26	0.04	0.96	0.00	0.52	0.80	n.d.[h]
2	1-butene	**2.2**	202	18.9	1.34	0.02	0.93	0.05	0.85	0.95	90.1
3[i]	1-butene	**2.2**	229	21.2	1.40	0.03	0.90	0.07	0.86	0.95	85.0
4	1-butene	**2.3**	188	36.5	1.36	0.05	0.93	0.02	0.72	0.89	77.8
5	1-butene	**2.4**	290	36.0	1.49	0.04	0.95	0.01	0.76	0.91	84.9
6[j]	1-pentene	**2.2**	224	22.5	1.33	0.00	0.90	0.06[k]	0.84	0.95	n.d.[h]

[a]3.0 ± 0.2 g 1-butene, 10 μmol of Ni complex in 2 mL CH_2Cl_2, 100 equiv. PMAO-IP; t_{rxn} = 24 h, T_{rxn} = -40 ∞C. [b]Determined by gel permeation chromatography at 135 °C in 1,2,4-trichlorobenzene versus polyethylene standards. [c]Determined by the equation $\chi_{4,1}$ = [(1-2R)/(1+2R)], where R = $[CH_3]/[CH_2]$, determined by ^{1}H NMR spectroscopy. [d]Determined using ^{13}C NMR spectroscopy. [e]Probability factor of three consecutive 4,2-units, determined from the equation [*mm*] = $\alpha^3+(1-\alpha)^3$. [f]Determined by differential scanning calorimetry, 2nd heat cycle. [g]Data retrieved from reference 3. [h]None detected. [i]8.0 ± 1.0 g 1-butene. [j]10 mL 1-pentene, 3 mL CH_2Cl_2 used. [k]Other 4% of regioerrors contribute to ethyl branches after incomplete chain-walking.

2.2.3 Polymerization of 1-Butene

2.2.3.1 Microstructure

The 4,2-poly(1-butene) produced by catalysts **2.2-2.4** demonstrates a significantly higher degree of regio- and stereocontrol than the polymer produced by **2.1** (Table 2.2, entries 1-4). Consequently, through differential scanning calorimetry (DSC) we observed melting transitions p to 90 °C and endotherms indicative of glass transitions between -52 and -57 °C. The effect of the steric environment of the aryl substituents on the regiochemistry of the polymerizations is not as significant as the effect of monomer loadings and concentrations (Table 2.2, entries 2 and 3). The polymer tacticities, however, are affected by both reaction conditions and ligand environment. Catalyst **2.2** gave a higher degree of stereocontrol than catalyst **2.3**, suggesting that ligand sterics strongly influence proper enantioface coordination and insertion (Table 2.2, entries 2 and 4). The overall degree of stereocontrol, which is obtained by measuring the percentage of three successive isotactic 4,2-units (Figure 2.1) ([*mm*] = 0.72-0.86), is considerably higher than that observed for the polymerization of *trans*-2-butene ([*mm*] = 0.41-0.64) (Scheme 2.5).[5] Fluorinated catalyst **2.4** yields a material with higher [*mm*] content in the polymer when compared to its methylated counterpart, **2.3** (Table 2.2, entries 4 and 5), suggesting that the electronic properties of the ligand also influence polymer microstructure.[11]

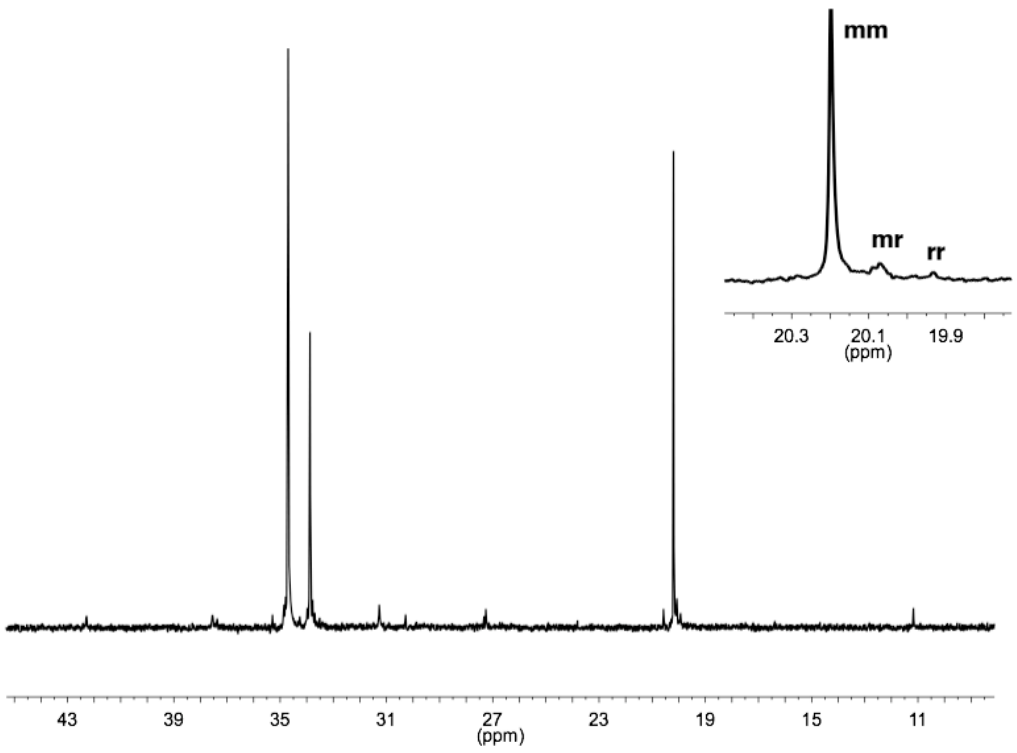
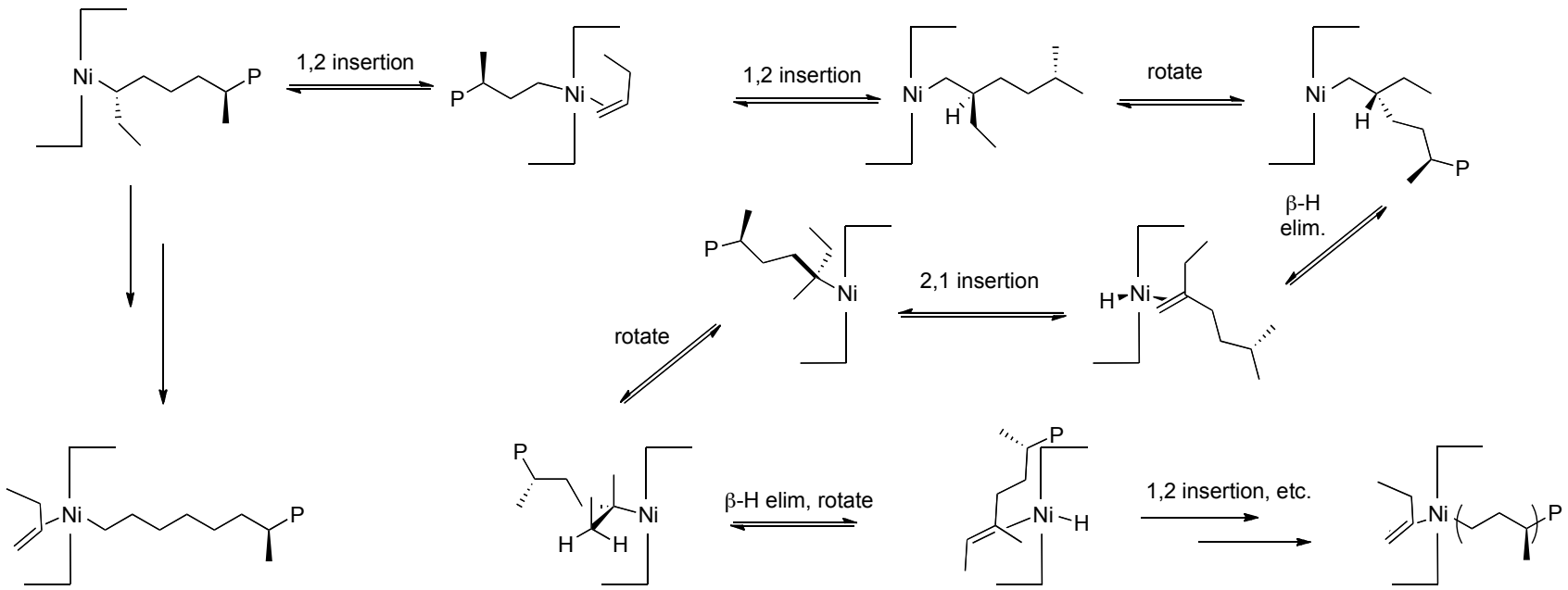


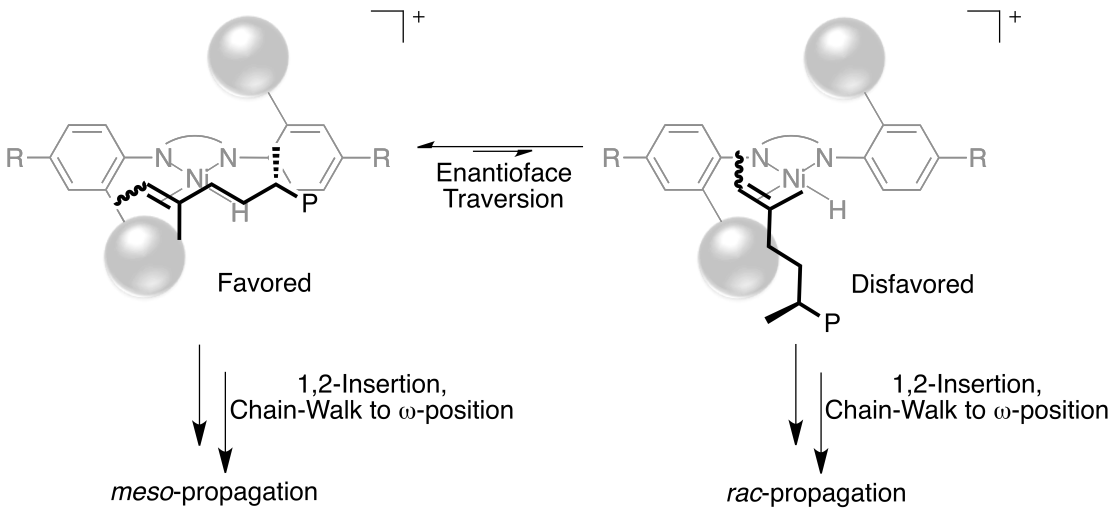
Figure 2.1 ^{13}C NMR spectra (1,1,2,2-$C_2D_2Cl_4$, 125 MHz, 135 °C) of 4,2-poly(1-butene) produced by catalyst **2.2** (Table 2.2, entry 2).



Scheme 2.3 Proposed mechanism for isoselective enchainments of 1-butene. C_2-symmetric ligand environment simplified for ease of viewing.

2.2.3.2 Proposed Mechanism of Isoselective Enchainments

In addition to initial enantioface coordination, which is primarily dictated by the steric environment, the stereochemistry can also be altered at the second β-H elimination of the chain-walking process (Scheme 2.3). The metal can eliminate from one of two hydrogens, also presumed to be mediated by sterics, which leaves a tertiary alkene-appended metal hydride intermediate. At this point we hypothesize that enantioface traversion is the other source of stereodefects, and this event is minimized with catalyst **2.4** due to tighter binding of the olefin to the more electron-deficient metal center (Scheme 2.4).[12]



Scheme 2.4 Proposed source of stereoerror formation in chain-walking polymerization of 1-butene.

2.2.3.3 Thermal Properties of iso*-4,2-Poly(1-butene)*

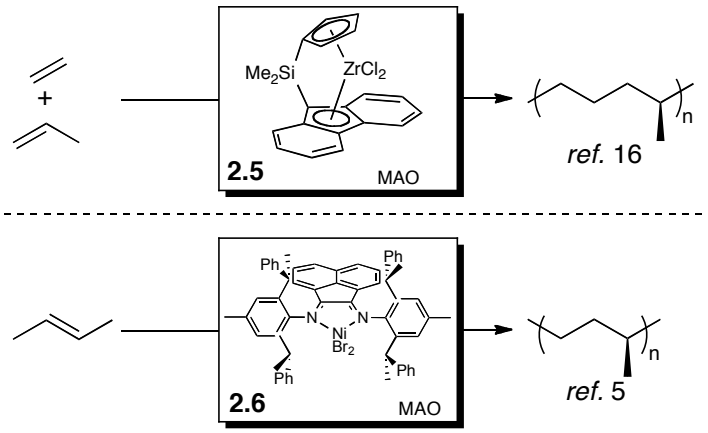
The thermal properties of 4,2-poly(1-butene) are influenced by both tacticity and branch composition. Ethyl branching can be present as a result of subsequent 1,2-

insertions of monomer without chain-walking and would afford a polymer with lower melting transitions (Table 2.2, entry 3). Branches longer than a methyl are the typical contributors to amorphous polyethylene and could considerably reduce crystallinity relative to comonomer incorporation.[13] When ethyl branching is minimized in our 1-butene systems, an increased melting temperature is observed (Table 2.2, entry 2). The presence of 4,1-insertions (< 5%) is produced by a full chain-walking sequence after a 2,1-insertion to produce a diethylene fragment. It is not fully understood whether or not a small amount of this regiodefect can adversely effect the material's crystallinity.[14] However, recent collaborative studies have shown that isotactic polypropylene with < 5% 3,1-insertions, made with similar cumyl-substituted catalysts, had retained most of its crystallinity.[15]

2.2.4 Polymerization of 1-Pentene

The ω,2-enchainment polymerizations of α-olefins higher than 1-butene previously produced polymer with lower isotacticity.[3] 5,2-Poly(1-pentene) produced by catalyst **2.2**, however, exhibits predominantly ω,2-enchainment of olefin along with high tacticity ([*mm*] = 0.84) (Table 1, entry 6), which is structurally equivalent to the previously reported *iso*-poly(ethylene-*alt*-propylene) (Scheme 2.5), produced by the zirconocene/MAO catalyzed alternating copolymerization of ethylene and propylene ([*mm*] = 0.80).[16] The ethyl and propyl branching present (ca. 7 and 3%, respectively) is speculated to be a result of incomplete chain-walking. Although the [*mm*] content is high, the considerable branching in the 1-pentene system affords a polymer with no detectable melt transition and a low T_g (-62.4 °C), similar to the

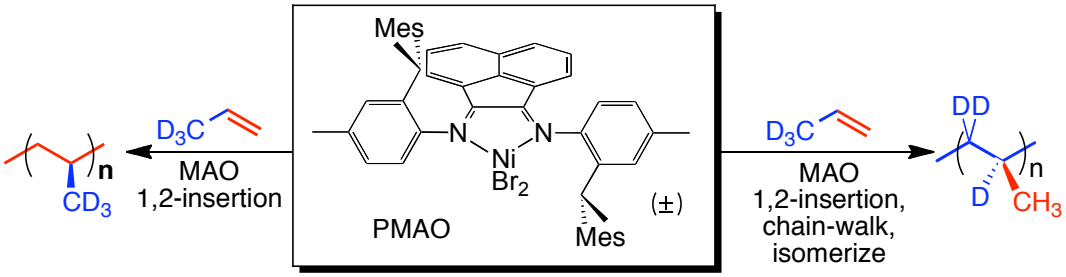
poly(ethylene-*alt*-propylene) polymers produced by Waymouth and coworkers (T_g = -54-56 °C).



Scheme 2.5 Previously reported syntheses of structural equivalents of isotactic ω,2-poly(α-olefin)s.

2.2.5 Deuterated Propylene Study

To determine if this regioselective chain-walking process is a consequence of the sterics of higher α-olefins, or whether it is an inherent trait of these specific catalysts, a polymerization of [3-d_3]propylene at -78 °C was performed using catalyst **2.1**.[10] We observed no change in the deuterium labels on the methyl position of the polypropylene, which demonstrates that the polymer chain does not undergo β-D elimination and subsequent chain-walking after every insertion of propylene (Scheme 2.6). This suggests the steric influence of higher α-olefins causes destabilization of the propagating species and favors β-H elimination to promote chain-walking.



Scheme 2.6 Proposed enchainment pathways for propylene by **1** at low temperatures.

2.3 Conclusions

In summary, 1-butene can be iso- and regioselectively polymerized via nickel(II) catalyzed 4,2-enchainment polymerization to produce semi-crystalline 4,2-poly(1-butene). Catalyst modification suggests that the mechanism of stereoerror formation is influenced by both the steric and electronic features of the catalyst. *Iso*-5,2-poly(1-pentene) can also be produced in the same manner from 1-pentene, albeit with slightly higher branching content. Additional catalyst development is currently in progress to further improve this unique process and explore new monomers.

2.4 Experimental

2.4.1 Complex Synthesis

General Methods. All manipulations of air- and/or water-sensitive compounds were carried out under dry nitrogen using a Braun UniLab drybox or standard Schlenk techniques. NMR spectra were acquired using either a Varian Mercury (300 MHz) or a Varian UnityInova (400 MHz) and were referenced either versus residual nondeuterated solvent solvent shifts (^{1}H, ^{13}C) or versus a hexafluorobenzene external standard (^{19}F). NMR data were acquired with the pulse sequences supplied in Vnmrj

2.1B/Chempack 4.1 and were processed and analyzed using the MestReNova 5.3 software package (2008, Mestrelab Research S. L.). Elemental analyses were performed by Robertson Microlit Laboratories, Inc. Madison, New Jersey. The LDI mass spectrum was recorded using a Waters MALDI Micro MX system. The sample was prepared by using the dried droplet method with no matrix present. Ionization was by a 257 nm UV nitrogen laser and the accelerating potential was 17.2 keV. The spectrum was recorded using the reflectron in positive ion mode. At 135 °C in 1,1,2,2-tetrachloroethane-d_2 the $^{13}C\{^1H\}$ NMR spectra of polymers were recorded using a Varian Unity Inova (600 MHz) spectrometer equipped with a 10 mm broadband probe and referenced versus residual non-deuterated solvent shifts. Molecular weights (M_n and M_w) and polydispersities (M_w/M_n) were determined by high temperature gel permeation chromatography (GPC) using a Waters Alliance GPCV 2000 GPC equipped with a Waters DRI detector and viscometer. The column set (four Waters HT 6E and one Waters HT2) was eluted with 1,2,4-trichlorobenzene containing 0.01 wt. % di-*tert*-butylhydroxytoluene (BHT) at 1.0 mL/min at 135 °C. Data were calibrated using monomodal polyethylene standards. Polymers were placed in a 135 °C oven for 24 h prior to molecular weight measurements. Polymer melting points (T_m) and glass transition temperatures (T_g) were measured by differential scanning calorimetry (DSC) using a TA Instruments Q1000 calorimeter equipped with an automated sampler. Analyses were performed in crimped aluminum pans under nitrogen and data were collected from the second heating run at a heating rate of 10 °C/min from -100 to 200 °C, and processed with TA Q series software. Procedures for the polymerization of 1-pentene[3] (Table 1, Entry 5)[i] and the polymerization of [3-

d_3]propylene by **2.1** have been previously reported. [9-10]

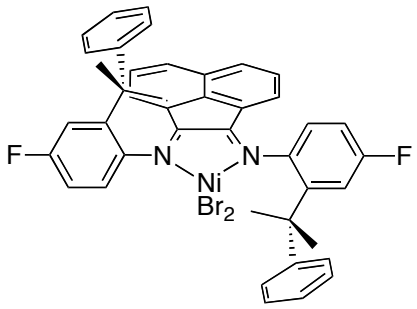
Materials. Toluene and hexanes were purified over columns of alumina and copper (Q5). Methylene chloride was purified over an alumina column and degassed by three freeze-pump-thaw cycles before use. Acenaphthenequinone (Alfa Aesar), α-methylstyrene (Aldrich), 4-fluoroaniline (Aldrich), formic acid (Aldrich), trifluoromethanesulfonic acid (Aldrich), and (dimethoxyethane)$NiBr_2$ ((DME)$NiBr_2$, Aldrich) were used without further purification. PMAO-IP (13 wt % Al in toluene, Akzo Nobel) was dried *in vacuo* to remove residual trimethylaluminum and used as a solid white powder. 1-Butene (Aldrich) was stored in an OxiClear rechargeable gas purifier model number RGP-R1-300B for at least 24 h prior to usage. Catalysts **2.1**, **2.2**, and **2.3** were synthesized as previously reported.[9-10]

4-Fluoro-2-(2-phenylpropan-2-yl)aniline (AN-2.4). CF_3SO_3H (1.06 mL, 12.0 mmol) was added to a mixture of 4-fluoroaniline (2.47 g, 60.0 mmol) and α-methylstyrene (7.14 mL, 60.0 mmol). The mixture was heated to 160 °C and allowed to react for 20 hours. The crude product was chromatographed on silica (95:5 hexanes:ethyl acetate) to give a dark purple oil (4.28 g, 31% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.34-7.17 (m, 6H, ArH), 6.79 (m, 1H, ArH), 6.46 (dd, J = 5.23 Hz, J = 8.62 Hz, 1H, ArH), 3.02 (broad s, 2H, NH_2), 1.67 (s, 6H, $C(CH_3)_2$). $^{13}C\{^1H\}$NMR ($CDCl_3$, 100 MHz): δ 156.45 (d, J_{CF} = 234.7 Hz), 148.57, 140.55 (d, J_{CF} = 2.2 Hz), 135.29 (d, J_{CF} = 5.6 Hz), 128.97, 126.48, 125.88, 118.08 (d,

J_{CF} = 7.7 Hz), 113.69 (d, J_{CF} = 1.9 Hz), 113.47, 42.43 (d, J_{CF} = 1.1 Hz), 28.92. ^{19}F NMR ($CDCl_3$, 380 MHz): δ -129.36 (m, ArF).

***rac*-ArN=C(An)C=NAr (Ar = 4-flouro-2-(2-phenylpropan-2-yl)phenyl; An = acenaphthene) (L-2.4).** In a sealed vial a mixture of **AN-2.4** (0.757 g, 3.30 mmol), acenaphthenequinone (0.300 g, 1.65 mmol), and formic acid (7 drops) in isopropanol (5mL) was heated and stirred at 80 °C for 4h. The product was filtered, washed with methanol, and dried *in vacuo* to afford a bright yellow solid (0.388 g, 19%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, J = 8.2 Hz, 2H, ArH), 7.38 (d, J = 9.4 Hz, 2H, ArH), 7.18 (t, J = 7.7 Hz, 2H, ArH), 7.12-6.95 (m, 6H, ArH), 6.73 (dd, J = 8.5, 5.6 Hz, 2H, ArH), 6.51 (d, J = 7.0 Hz, 6H, ArH), 6.19 (s, 2H, ArH), 1.81 (broad s, 12H, $C(CH_3)_2$). δ ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.15 (d, J_{CF} = 241.3 Hz), 159.79, 148.84, 146.69 (d, J_{CF} = 2.8 Hz), 141.26, 141.05 (d, J_{CF} = 6.1 Hz), 130.15, 128.61, 128.15, 127.13, 126.74, 126.59, 124.47, 123.34, 119.68, 114.46 (d, J_{CF} = 24.6 Hz), 113.50 (d, J_{CF} = 22.0 Hz), 42.91. ^{19}F NMR ($CDCl_3$, 375 MHz): δ -122.51 (broad s, ArF). Anal. Calc. for $C_{42}H_{34}F_2N_2$: C, 83.42; H, 5.67; N, 4.63. Anal. found: C, 83.18; H, 5.57; N, 4.59.

***rac*-(ArN=C(An)C=NAr)$NiBr_2$ (Ar = 4-flouro-2-(2-phenylpropan-2-yl)phenyl; An = acenaphthene) (3). L-2.4** (0.388 g, 0.642 mmol) and (DME)$NiBr_2$ (0.198 g, 0.0.642 mmol) were combined under N_2. CH_2Cl_2 was added to afford a dark red solution, which was allowed to stir overnight. The reaction mixture was filtered through Celite under N_2 and volatiles were then removed *in vacuo*. The crude red solid was redissolved in CH_2Cl_2 and layered with hexanes to afford a dark red microcrystalline solid (0.092 g, 17%). MALDI (m/z): 822.8.



2.4.2 Butene Polymerization

Typical Procedure for the Polymerization of 1-Butene (Table 1, entry 2). A Schlenk flask was charged with a stirbar and PMAO-IP (0.058 g, 1.0 mmol) under N_2. The 1-butene was condensed into the vessel at -40 °C. The solution was allowed to equilibrate at this temperature for 10 min. A 2 mL solution of catalyst **2.4** (9.2 mg), 10 μmol) in CH_2Cl_2 was then injected to initiate the polymerization. The reaction was quenched with MeOH, and the polymer was precipitated out of a plentiful amount of acidic methanol (2% HCl(aq)), followed by stirring of the suspension overnight. The polymer was filtered, washed with methanol, and dried to constant weight *in vacuo* at 60 °C.

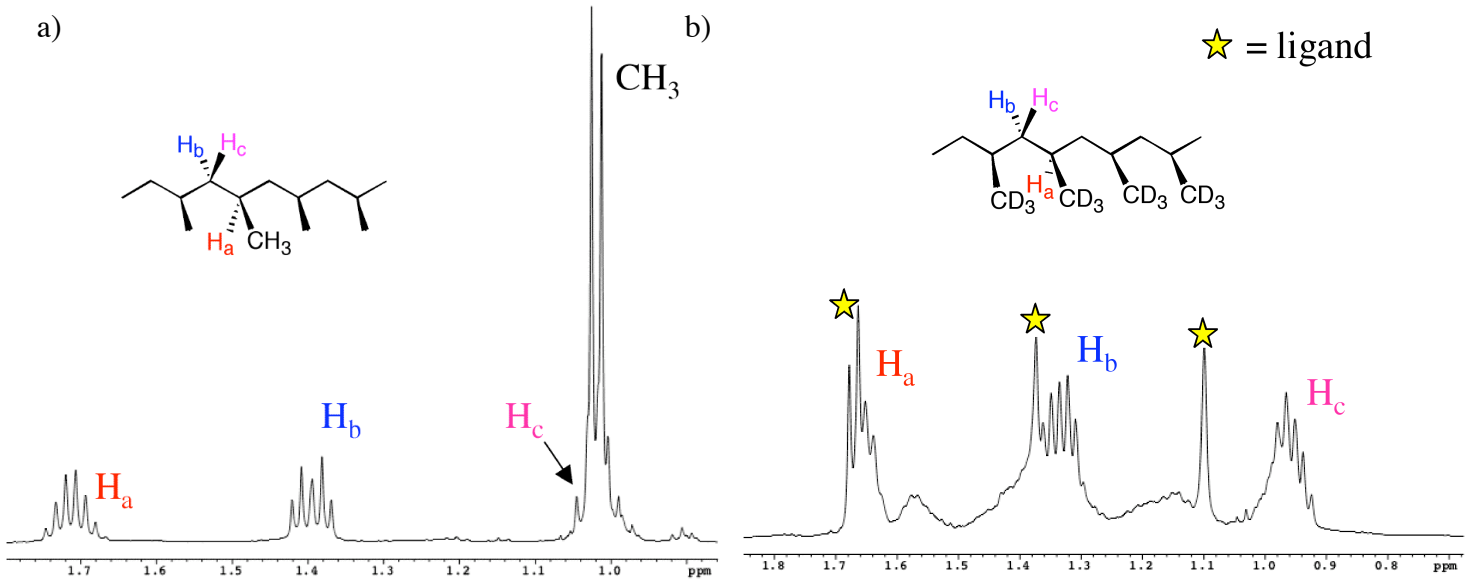


Figure 2.2 ^{1}H NMR Spectra (500 MHz, 90 °C, tetrachloroethane-d_2) of isotactic polypropylene (a) and polypropylene-d_3 made from **2.1**/MAO at –78 °C (b).

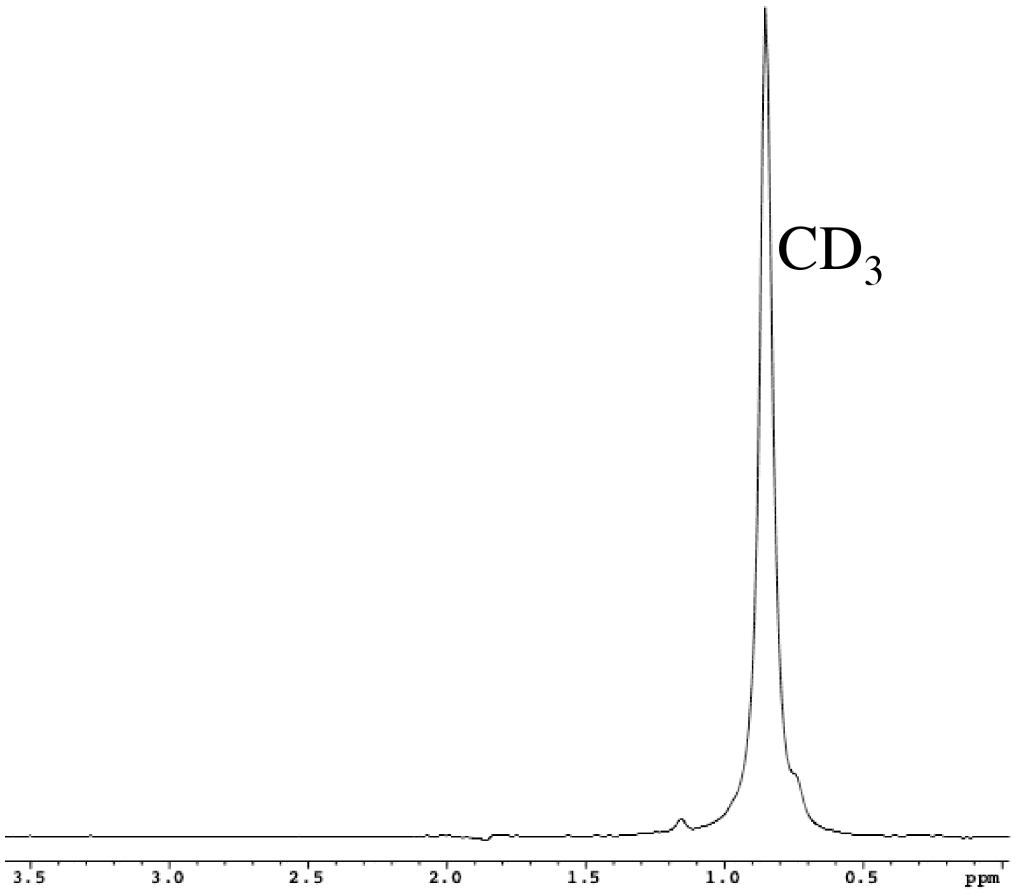


Figure 2.3 ^{2}H NMR Spectrum (500 MHz, 90 °C, tetrachloroethane-d_2) of polypropylene-d_3 made from **2.1**/MAO at –78 °C.

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CHAPTER THREE

Enhanced Ethylene Polymerization Activity of a Neutral Cumyl-Derived Amidinate Nickel (II) Catalyst: Influences of Sterics and Cocatalysts

3.1 Introduction

Brookhart's discovery of nickel and palladium catalysts for olefin polymerization[1] was a major breakthrough in the field of non-metallocene olefin polymerization catalysis.[2] The functional group tolerance and the unique "chain-walking" polymerization mechanism of these catalysts have spawned a multitude of new polymer architectures that comprise materials with new physical properties.[3] The modular α-diimine backbone of the Brookhart complexes incorporate bulky substituents that blocked the axial sites of the active square planar metal center to inhibit associative displacement of a growing chain. Although axially exposed catalysts are indeed valuable for higher α-olefin production,[4] the development of new sterically encumbered nickel-catalysts has provided for a variety of pathways to novel materials.[5,1f]

The mechanistic insights resulting from Brookhart's studies were ultimately translated to neutral nickel and palladium systems. In 1998, Grubbs and coworkers reported salicylaldimine nickel (II) complexes bearing large substituents on the ortho position of the phenol moiety, which provided sufficient protection from chain transfer.[6] The steric protection is aided by the presence of a six-membered ring chelate, which results in the ligand substituents providing increased steric protection relative to systems with smaller chelates. This work led to a surge of discoveries of six-membered chelates active for olefin polymerizations.[7] Some of these catalysts can insert functional comonomers[8] or can be utilized in aqueous conditions.[7a,7f] Their

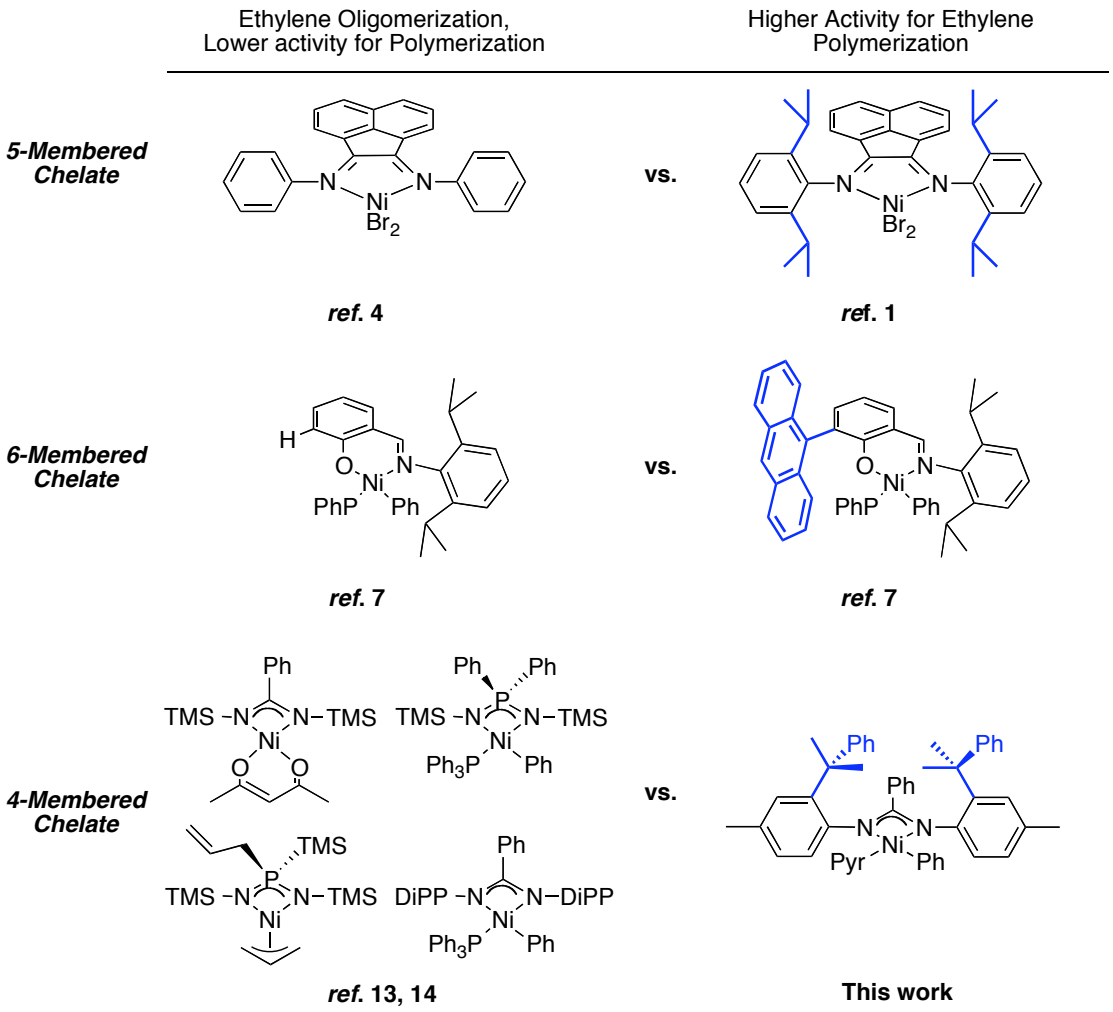
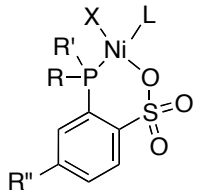
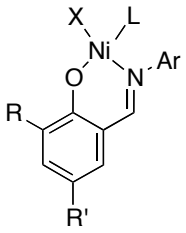


Figure 3.1 Various complexes and their bulky derivatives for the oligomerization and polymerization of ethylene.

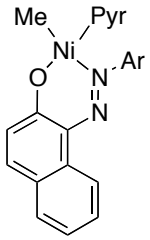
ligand and electronic effects on polymerization behavior have also been investigated.[9] These studies confirm the proportionality of catalyst activity to ligand sterics, as well as electron deficiency. Five-membered nickelocycles have also been demonstrated to be viable neutral nickel catalysts, including α-amidoketone (N-O) complexes[10] and modified P-O complexes,[11] originally used in the Shell higher olefin process (SHOP).



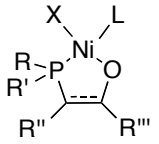
***ref.* 7i, 7j, 7m, 7o**



***ref.* 6, 7f, 7h, 8, 10a, 10c**



***ref.* 7b**



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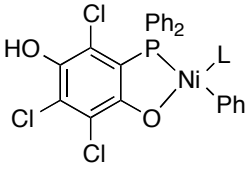

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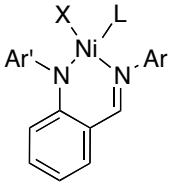

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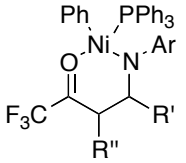

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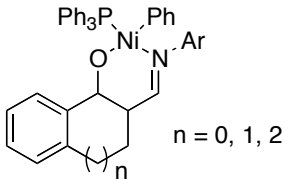

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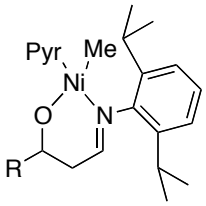

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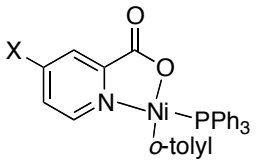

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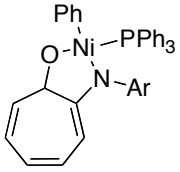

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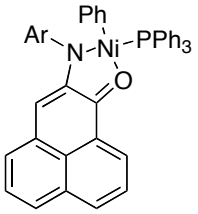

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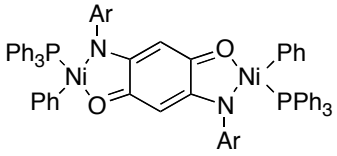

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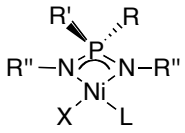


ref. 12

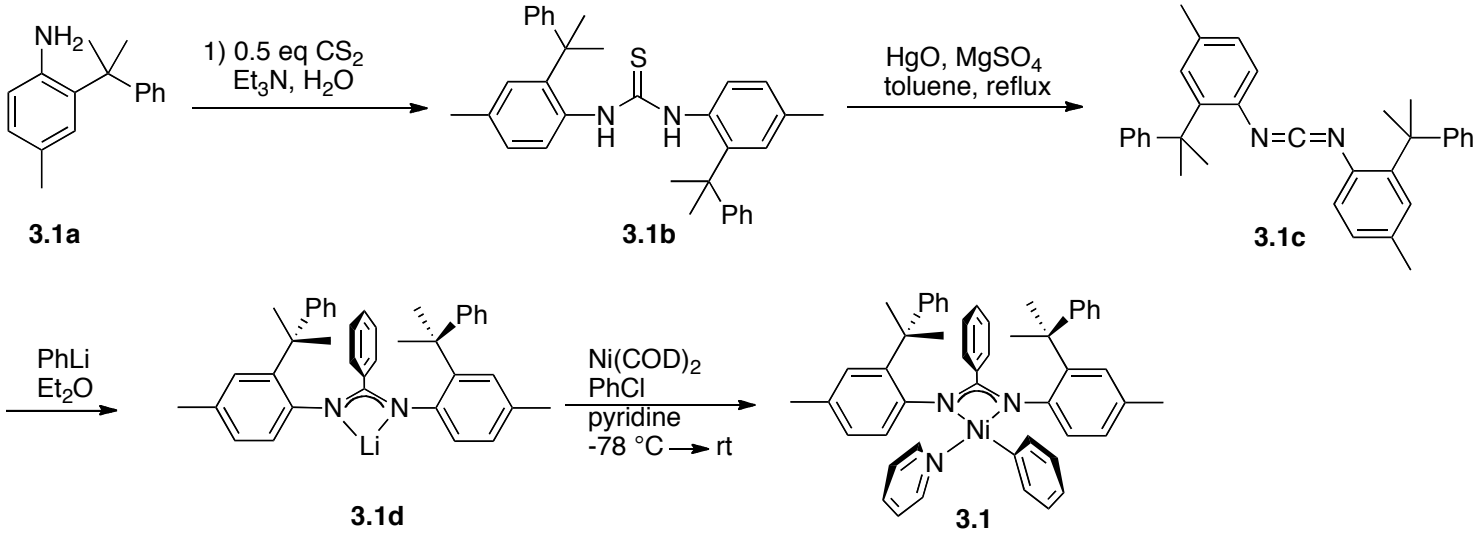
Figure 3.2 Notable classes of neutral nickel complexes for the polymerization of ethylene. Anionic X-type donors, neutral L-type donors, and R-substituents indicate modularity of the complexes.

The design of analogous four-member metallacycles for use in olefin polymerization is challenging. The more open geometry of the metallacycle allows for facile displacement of the growing polymer chains, which result in the formation of oligomers, low molecular weight polymers, or rapid catalyst deactivation. Examples include iminophosphonamido nickel complexes, which oligomerize or polymerize ethylene with low to moderate activities.[12] Recently, amidinate ligands have emerged as versatile ligands for transition metal-mediated processes, including olefin polymerizations.[13] However, neutral amidinate nickel and related complexes have demonstrated limited success in olefin polymerization. These catalysts have been reported to oligomerize ethylene or propylene, or produce polyethylene (PE) with very low activities.[13, 14] Consequently, we envisioned a sterically hindered amidinate ligand which would block the axial coordination sites of the square-planar nickel center to discourage chain termination in the polymerization. Herein is reported a bulky neutral cumyl-derived amidinate nickel catalyst that exhibits higher ethylene polymerization activity than previously reported amidinate nickel complexes. We also report an unusual cocatalyst effect in the presence of copper (II) bromide.

3.2 Results and Discussion

3.2.1 Synthesis and Structure

We have previously utilized anilines containing bulky cumyl moieties at the ortho position as useful substituents in cationic α-diimine nickel (II) systems.[5e] A similar approach was used for the synthesis of a sterically hindered Ni(II) amidinate complex.



3.1a **3.1b** **3.1c** **3.1d** **3.1**

Scheme 3.1 Synthesis of complex **3.1**.

The reaction between ortho-cumyl aniline **3.1a** and carbon disulfide in the presence of triethylamine and water produced the N-arylated thiourea **3.1b**. Without further purification, a subsequent mercury oxide promoted dehydrosulfination of the crude thiourea in refluxing toluene afforded the carbodiimide **3.1c** as a beige solid in 25% yield after recrystallization (Scheme 3.1).[15] Phenyllithiation of the carbodiimide in ether yielded the lithium amidinate **3.1d**. The reaction of this amidinate with phenylnickel(II) chloride (generated *in situ* from bis(cyclooctadiene)nickel(0) and chlorobenzene) in the presence of pyridine at low temperatures[16] yielded **3.1** as an orange compound in 16% yield.

The solid-state structure of **3.1**, determined by single crystal X-ray diffraction, is shown in Figure 3.2. The structure shows encumbrance of the cumyl moieties around the square-planar nickel center. We hypothesize that this steric bulk prevents associative displacement of the growing chain to give polymer with higher molecular weights. A more detailed structural analysis of the metal coordination geometry in solution phase was also performed. ^{1}H NMR rotating frame Overhauser effect spectroscopy (ROESY) was used to probe the spatial arrangement of ligand components around the metal center. Figure 3.3 depicts the relevant through-space couplings and observed exchange spectroscopic (EXSY) correlations as green and blue arrows, respectively. Consistent with the solid-state structural features, the cumyl phenyl groups are oriented so that they are away from the plane formed by the metallacycle. **Ph^{1}** resides near the backbone aryl and **Ph^{2}** situates near the nickel-appended phenyl. In this conformation, the methyl groups block the axial coordination sites.

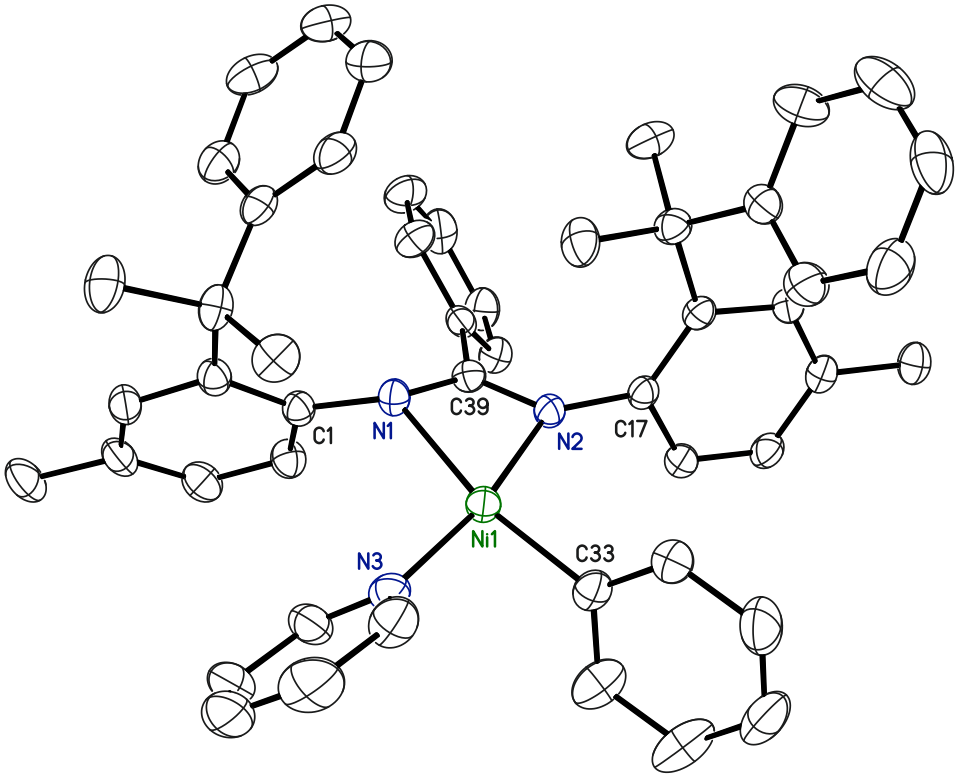


Figure 3.3 ORTEP diagram of catalyst **3.1** (molecules of crystallization omitted). Hydrogen atoms are omitted for clarity, and ellipsoids are drawn at the 40% probability level.

Table 3.1 Selected Bond Lengths (Å) and Angles (°) of catalyst **3.1**

Ni-N(1)	2.0313(17)
Ni-N(2)	1.8843(14)
Ni-N(3)	1.8816(16)
Ni-C(33)	1.880(2)
N(1)-C(1)	1.427(3)
N(1)-C(39)	2.3479(19)
N(2)-C(17)	1.423(2)
N(2)-C(39)	1.317(2)
N(1)-C(39)-N(2)	109.57(17)
N(1)-Ni-N(3)	101.61(7)
N(2)-Ni-C(33)	98.81(8)
N(3)-Ni-C(33)	92.25(9)
N(3)-Ni-N(2)	168.38(7)

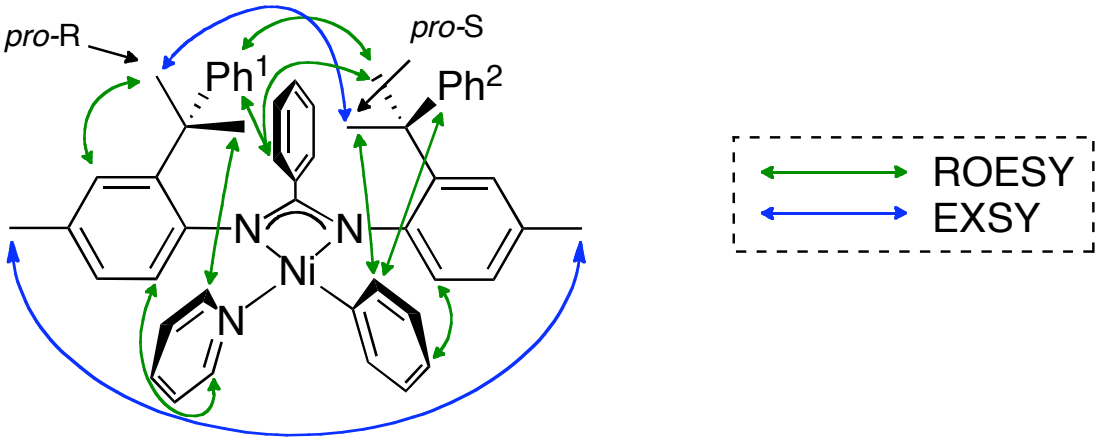


Figure 3.4 Relevant ROESY and EXSY correlations of complex **3.1** (600 MHz, C_6D_6).

The presence of exchange signals in the two-dimensional spectrum indicates that the pyridine and the anionic phenyl ligands must switch positions in order to reverse the magnetic environments. We speculate that this coordination site traversion may proceed through a tetrahedral transition state, which may be feasible given the open coordination environment of a four-membered chelate.[17] The exchange of the ROESY signals of the *pro*-R and the *pro*-S methyl groups on their respective cumyl substituents also indicate that upon coordination site interchange, subsequent rotation of the cumyl fragments ensues to create the same ligand conformation about the nickel center.

Complex **3.1** undergoes C-H activation of a cumyl methyl substituent at room temperature in solution yielding complex **3.2**. An X-ray crystal structure (Figure 3.3) and appropriate two-dimensional NMR analysis (see Experimental) had confirmed the proposed structure. Presumably, the proximity of the anionic phenyl ligand to the *pro*-S methyl, indicated by their through space correlations (*vide supra*), allows for the

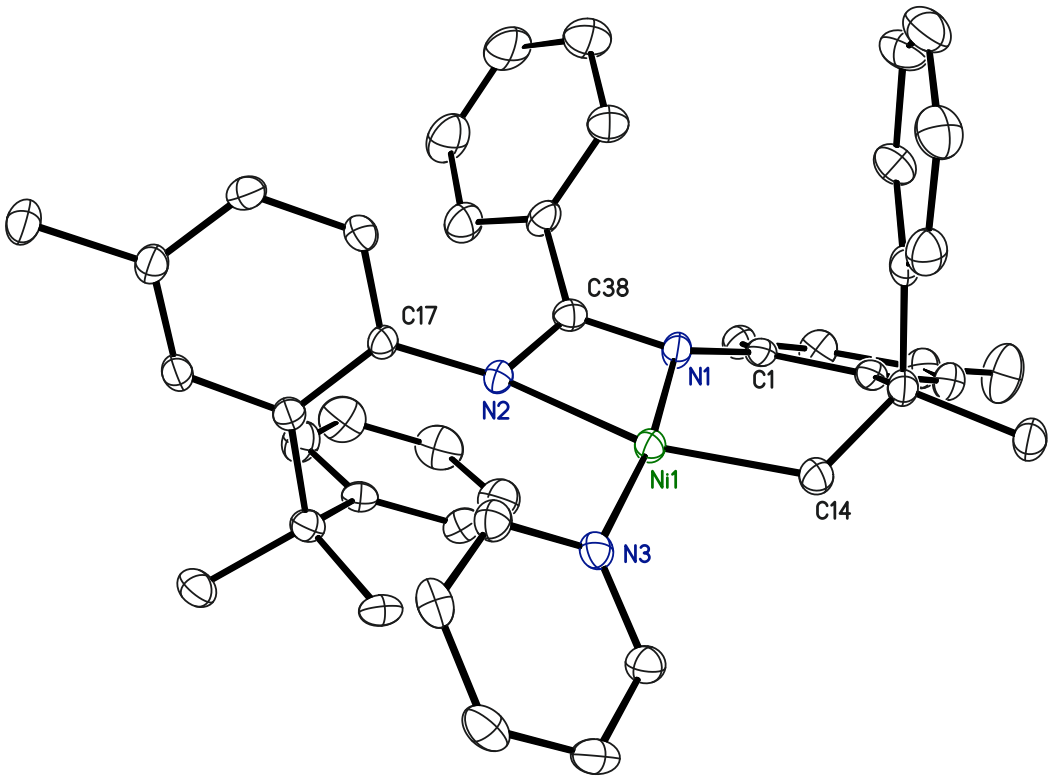


Figure 3.5 ORTEP diagram of complex **3.2** (molecules of crystallization omitted). Hydrogen atoms are omitted for clarity, and ellipsoids are drawn at the 40% probability level.

Table 3.2 Selected Bond Lengths (Å) and Angles (°) of complex **3.2**

Ni-N(1)	1.8362(15)
Ni-N(2)	2.1232(14)
Ni-N(3)	1.9014(15)
Ni-C(14)	1.9139(18)
N(1)-C(1)	1.395(2)
N(1)-C(38)	1.351(2)
N(2)-C(17)	1.421(2)
N(2)-C(38)	1.326(2)
N(1)-C(38)-N(2)	61.40(9)
N(1)-Ni-N(2)	66.61(6)
N(1)-Ni-C(14)	91.78(7)
N(3)-Ni-C(14)	96.15(7)
N(3)-Ni-N(2)	105.44(6)

abstraction of a methyl hydrogen, resulting in loss of benzene and formation of a stable six-membered nickelocycle. Such cyclometallation is one catalyst degradation pathway and has been observed in related Ni and Pd systems.[18] Occurrence of such an event provides crucial information about future ligand designs.

3.2.2 Ethylene Polymerization Activity

The polymerization of ethylene by **3.1** was investigated, and the results of these polymerizations are shown in Table 3.3. The effect of the bulky amidinate ligand was substantial. As predicted, a substantial increase in activity and molecular weight compared to the less bulky amidinate catalysts reported previously.[14] However, very broad molecular weight distributions were observed when methylaluminoxane (MAO) was employed as the sole scavenger/cocatalyst (Table 1, entries 1-3).[19] We originally speculated that competitive binding of the pyridine to the nickel versus ethylene would broaden the molecular weight distributions. However, the broad distributions and lower activity were observed when $Ni(COD)_2$ was added as a Lewis base scavenger (Table 3.3, entry 2). Copper (II) complexes were tested since they have been reported to be efficient pyridine scavengers.[20] The polymerization reaction in the presence of two equivalents of copper sulfate (Table 3.3, entry 3) showed similar behavior as the system utilizing $Ni(COD)_2$. However, the addition of copper (II) bromide results in higher activity and unimodal molecular weight distributions (Table 1, entries 4 and 5). Based on their high melting transitions, the polyethylenes formed by this catalyst are quite linear, indicative of the reduced chain-walking behavior common for neutral

Table 3.3 Ethylene polymerization behavior of complex **3.1**.[a]

entry	cocatalyst	T_{rxn} (°C)	t_{rxn} (h)	TON	TOF (h^{-1})	M_n (theo) (kDa)	M_n (exp) (kDa)[b]	M_w/M_n[b]	T_g[c] (°C)	T_m[c] (°C)
1	PMAO-IP	0	2	959	479	25.0	bimodal	bimodal	44.2	128
2	PMAO-IP, $Ni(COD)_2$ (2eq)	0	2	529	264	13.8	bimodal	bimodal	n.d.[d]	123
3	PMAO-IP, $CuSO_4$ (2eq)	0	2	542	271	14.1	bimodal	bimodal	42.4	119
4	PMAO-IP, $CuBr_2$ (2eq)	0	2	2620	1310	68.0	81.0	1.88	n.d.	124
5	PMAO-IP, $CuBr_2$ (2eq)	-20	3	2750	917	71.5	203	1.93	n.d.	134

[a]100 psi Ethylene, 25 mL toluene, 20 μmol of **1**, [Al]/[Ni] = 150. [b]Determined by gel permeation chromatography at 135 °C in 1,2,4-trichlorobenzene versus polyethylene standards. [c]Determined by differential scanning calorimetry, 2nd heat cycle. [d]None detected.

nickel catalysts. At low temperature, minimal chain walking occurs, which is reflected in a nearly linear PE. (Table 1, entry 5)

The substantial difference of activity and molecular weight distribution of reactions in the presence of copper (II) bromide versus copper sulfate and $Ni(COD)_2$ raises the question of whether copper (II) bromide is not simply acting as a pyridine scavenger. One possible alternative role is that copper (II) bromide prevents reduction of the nickel catalyst by MAO, maintaining a single active Ni(II) propagating species. Nagel and coworkers have reported analagous copper (II) mediated radical polymerizations of acrylates in the presence of MAO and proposed that a Cu(II) to Cu(I) reduction by excess MAO formed the active catalysts.[21] Consequently, in absence of copper (II) bromide, a second active site may be responsible for the observed bimodal behavior and decreased activities in our ethylene polymerizations. To the best of our knowledge, this is the first instance of a copper based reagent greatly enhancing the activity of a nickel mediated ethylene polymerization. Future investigations will study the effect of copper (II) bromide in more detail in order to elucidate its role in the polymerization [22]

3.3 Conclusion

In summary, rational catalyst design has led to the development of an active neutral amidinate nickel catalyst for the polymerization of ethylene. X-ray crystallography and two-dimensional NMR spectroscopy revealed that the bulky cumyl fragments on the amidinate effectively block the axial sites.. This steric crowding prevents associative displacement of the growing polymer chain and results in higher catalyst activities and polymer molecular weights than were observed in previously reported four-membered

nickel chelates. Polymerizations conducted in the presence of copper (II) bromide as a cocatalyst showed higher activities and narrower molecular weight distributions; we propose that Cu(II) prevents reduction of the catalyst to an inactive species. Information from these studies will be used for future catalyst and cocatalyst design.

3.4 Experimental

*3.4.1 Synthesis of **3.1***

General Methods. All manipulations of air- and/or water-sensitive compounds were carried out under dry nitrogen using a Braun UniLab drybox or standard Schlenk techniques. NMR spectra of the ligand were acquired using a Varian Inova (400 MHz) and were referenced versus residual nondeuterated solvent solvent shifts. Complexes **3.1** and **3.2** were characterized by 1-D and 2-D NMR spectroscopy in C_6D_6 at ambient temperature on a Varian UnityInova (600 MHz for complex **3.1**, 500 MHz for complex **3.2**) spectrometer operating at 599.757 MHz for ^{1}H observation using a Varian inverse ^{1}H-{^{13}C, ^{15}N} triple-resonance probehead with triple-axis gradients. NMR data were acquired with the pulse sequences supplied in Vnmrj 2.2D/Chempack 4.1 (Agilent Inc.) and were processed and analyzed using the MestReNova 7.1 software package (2012, Mestrelab Research S. L.). Gradient selected COSY spectra were acquired using the gCOSY sequence with spectral widths of 4.2–4.8 kHz. A total of 512–600 points were collected in the indirectly detected dimension with 1 scan of 0.6–0.8s acquisition time per increment. The resulting matrices were zero filled to 2k x 4k complex data points in F1 and F2, respectively, and unshifted sine bell (F1), and simultaneous unshifted sine bell and 3 Hz Gaussian (F2) window functions were applied prior to Fourier transformation. ROESY spectra were acquired using the ROESYAD sequence with mixing times of

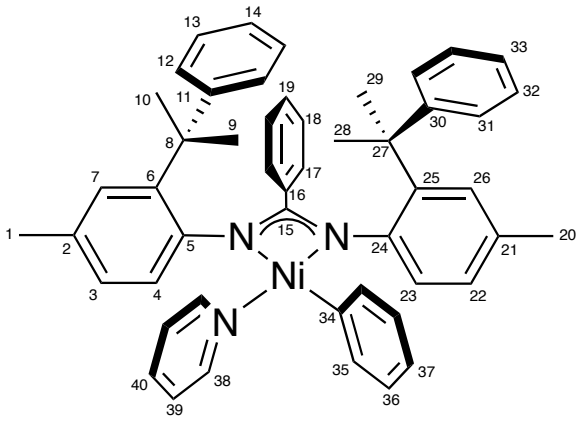
200ms and spectral widths of 4.2–4.8 kHz. A total of 300–600 complex points were collected in the indirectly detected dimension with 4 or 8 scans of 0.4s acquisition time per increment. The resulting matrices were zero filled to 2k x 2k complex data points and Gaussian window functions were applied in both dimensions prior to Fourier transformation. The multiplicity-edited HSQC spectrum was acquired with the HSQCAD sequence with spectral widths of 4.2 kHz and 25.1 kHz in the ^{1}H and ^{13}C dimensions, respectively. A total of 600 complex points were collected in the indirectly detected dimension with 4 scans of 0.15s acquisition time per increment. The resulting matrices were zero filled to 4k x 2k complex data points in F1 and F2, respectively, and a Gaussian window function was applied in the ^{1}H dimension prior to Fourier transformation. The HMBC spectrum were acquired in phase sensitive mode with the gHMBCAD sequence and optimized for 8 Hz couplings. Spectral widths were 4.2 kHz and 30.2 kHz in ^{1}H and ^{13}C dimensions, respectively. A total of 900 complex points were collected in the indirectly detected dimension with 4 scans of 0.3s acquisition time per increment. The resulting matrices were zero filled to 4k x 2k complex data points in F1 and F2, respectively, and simultaneous unshifted sine bell and 4 Hz Gaussian window functions were applied in the ^{1}H dimension prior to Fourier transformation. In order to improve ^{13}C resolution in the aromatic region, band-selective HSQC (bsHSQCAD) and HMBC (bsgHMBC) spectra were acquired with 5.3 kHz (120–155 ppm) and 8.3 kHz (120–175 ppm) spectral widths in the ^{13}C dimension, respectively, and ^{1}H spectral widths of 4.8 kHz. The bsHSQCAD spectrum was acquired with 600 complex data points in the indirect dimension with 4 scans of 0.15s acquisition time per increment. The resulting matrix was zero filled to 2k x 2k complex data points and a 3 Hz Gaussian window

function was applied in the ^{1}H dimension prior to Fourier transformation. The bsgHMBC spectrum was acquired with 800 complex data points with 8 scans of 0.3s acquisition time per increment. The resulting matrix was zero filled to 2k x 2k complex data points and simultaneous unshifted sine bell and 4Hz Gaussian window functions were applied in in the ^{1}H dimension prior to Fourier transformation. Molecular weights (M_n and M_w) and polydispersities (M_w/M_n) were determined by high temperature gel permeation chromatography (GPC) using a Waters Alliance GPCV 2000 GPC equipped with a Waters DRI detector and viscometer. The column set (four Waters HT 6E and one Waters HT2) was eluted with 1,2,4-trichlorobenzene containing 0.01 wt. % di-*tert*-butylhydroxytoluene (BHT) at 1.0 mL/min at 135 °C. Data were calibrated using monomodal polyethylene standards. Polymers were placed in a 135 °C oven for 24 h prior to molecular weight measurements. Polymer melting points (T_m) and glass transition temperatures (T_g) were measured by differential scanning calorimetry (DSC) using a Mettler Toledo Polymer DSC equipped with an automated sampler. Analyses were performed in crimped aluminum pans under nitrogen and data were collected from the second heating run at a heating rate of 10 °C/min from -70 to 200 °C, and processed with STARe series software.

Materials. Toluene and pentanes were purified over columns of alumina and copper (Q5). Diethyl ether was purified over an alumina column and degassed by three freeze-pump-thaw cycles. Pyridine was distilled from potassium hydroxide and sparged with nitrogen for 30 min. Chlorobenzene was distilled from phosphorus pentoxide and degassed by three freeze-pump-thaw cycles. Carbon disulfide (Aldrich), triethylamine (Aldrich), mercury oxide (Aldrich), magnesium sulfate (Fisher), phenyllithium (1.8M in

dibutyl ether) (Aldrich), bis(cyclooctadiene)nickel(0) ($Ni(COD)_2$, Strem), Copper Sulfate (Aldrich), and Copper Bromide (Aldrich) were used without further purification. PMAO-IP (13 wt % Al in toluene, Akzo Nobel) was dried *in vacuo* to remove residual trimethylaluminum and used as a solid white powder. Ethylene (Airgas, ultrahigh purity) was purified over columns of 3 Å molecular sieves (Aldrich) and copper Q5 (Engelhard Corporation). 2-(2-phenylisopropyl)-4-methylaniline used in the synthesis of **3.1** was prepared according to literature procedures.[5e]

N,N'-(2-(2-phenylisopropyl)-4-methylphenyl)carbodiimide (3.1c). According to a literature preparation,[15] 2-(2-phenylisopropyl)-4-methylaniline **3.1a** (12.7 g, 47.6 mmol), carbon disulfide (1.43 mL, 23.8 mmol), and triethylamine (6.63 mL, 47.6 mmol) were stirred in water (30 mL) at room temperature for 1 hour. The mixture was then heated at 80 °C and stirred overnight. The solution was extracted twice with methylene chloride and dried ($MgSO_4$). Volatiles were removed *in vacuo*, and the resultant thick yellow-green oil (**3.1b**) was used without further purification. Mercury oxide (10.3g, 47.6 mmol), magnesium sulfate (14.1 g, 57.1 mmol), and toluene (100 mL) were added to the oil and the suspension was refluxed overnight. After filtration through Celite, volatiles were removed by rotary evaporation to afford a dark brown oil. Recrystallization from CH_2Cl_2/MeOH afforded the pure compound as beige-colored needles (5.42 g, 24.8%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26-7.10 (m, 12H, ArH), 6.84, (dd, 2H, ArH), 6.14 (d, 2H, ArH), 2.34 (s, 6H, $ArCH_3$), 1.65 (s, 12H, $C(CH_3)_2$). ^{13}C{1H}NMR ($CDCl_3$, 100 MHz): δ 151.24, 142.31, 134.49, 134.20, 131.86, 127.98, 127.91, 127.52, 126.38, 126.12, 124.80, 42.57, 29.94, 21.47.



[Ar-N=C(Ph)-N-Ar]Ni(Ph)(Pyr) (Ar = 2-(2-phenylisopropyl)-4-methylphenyl) (3.1). Following a literature procedure,[16] phenyl lithium (1.8M/dibutyl ether) (1.2mL, (2.06 mmol) was slowly added to N,N'-(2-(2-phenylisopropyl)-4-methylphenyl)carbodiimide (945 mg, 2.06 mmol) in 20 mL of diethyl ether at ambient temperature under N_2 and stirred for 2-3 hours. The reaction mixture was rid of the solvent *in vacuo* and taken up in pyridine (10 mL). The red solution was then cannula transferred to a Schlenk flask charged with a stir bar and $Ni(COD)_2$ (567 mg, 2.06 mmol) in a liquid nitrogen bath to immediately be frozen. Once the mixture has been able to stir after being exposed to ambient temperatures, chlorobenzene (0.51 mL, 4.94 mmol) was added. Once warmed to room temperature, the reaction mixture turned dark red accompanied with black precipitate. After stirring overnight at room temperature, the reaction mixture was reduced to a few milliliters, taken up in pentanes, and filtered through Celite. The filtrate was reduced and allowed to stand overnight at room temperature to afford an orange powder with some deep orange crystals (250 mg, 16%). The ^{1}H, $^{13}C\{1H\}$, and relevant correlative NMR data obtained in C_6D_6 at room temperature are tabulated below. The resonances were assigned with the aid of COSY, HMBCAD, HSQCAD, and ROESY NMR experiments. Even after multiple

recrystallizations the compound exists in a large ratio to an unidentifiable, presumably related or isomeric, compound. Theoretical and experimental agreements of the molecular weights of synthesized polyethylenes formed indicate that this species does not contribute to the bulk of the active catalyst.

Table 3.4 NMR Data for complex **3.1**.

Carbon atom #	$^{13}C\{^{1}H\}$ NMR δ	^{1}H NMR δ	ROESY	EXSY
1	21.06	2.01	C7	C20
2	130.81	-		
3	127.33	6.67		
4	129.53	6.96	C38	
5	145.27	-		
6	143.94	-		
7	129.20	7.06	C1, C9, C10	
8	43.24	-		
9	27.99	1.84	C7, C38	
10	32.73	1.61	C7	C28
11	150.34	-		
12	127.44	7.46	C17	
13	127.96	7.19		
14	125.31	7.01		
15	170.34	-		
16	133.42	-		
17	130.02	6.63	C17, C28, C29	
18	127.35	6.67		
19	128.18	6.20		
20	20.73	1.69	C26	C1
21	132.61	-		
22	125.90	6.55		
23	131.72	7.14	C35	
24	141.01	-		
25	144.46	-		
26	132.29	6.61	C20, C29, C28	
27	45.34	-		
28	34.11	2.21	C17, C26, C35	C7
29	31.79	1.79	C17, C26, C31	
30	153.96	-		
31	127.08	7.21	C29	
32	127.99	7.20		
33	125.08	7.09		
34	152.69	-		
35	137.83	7.55	C23, C28, C31, C38	
33	125.47	6.98		
37	122.77	6.87		
38	151.64	8.05	C4, C9	
39	123.13	5.96		
41	135.39	6.42		

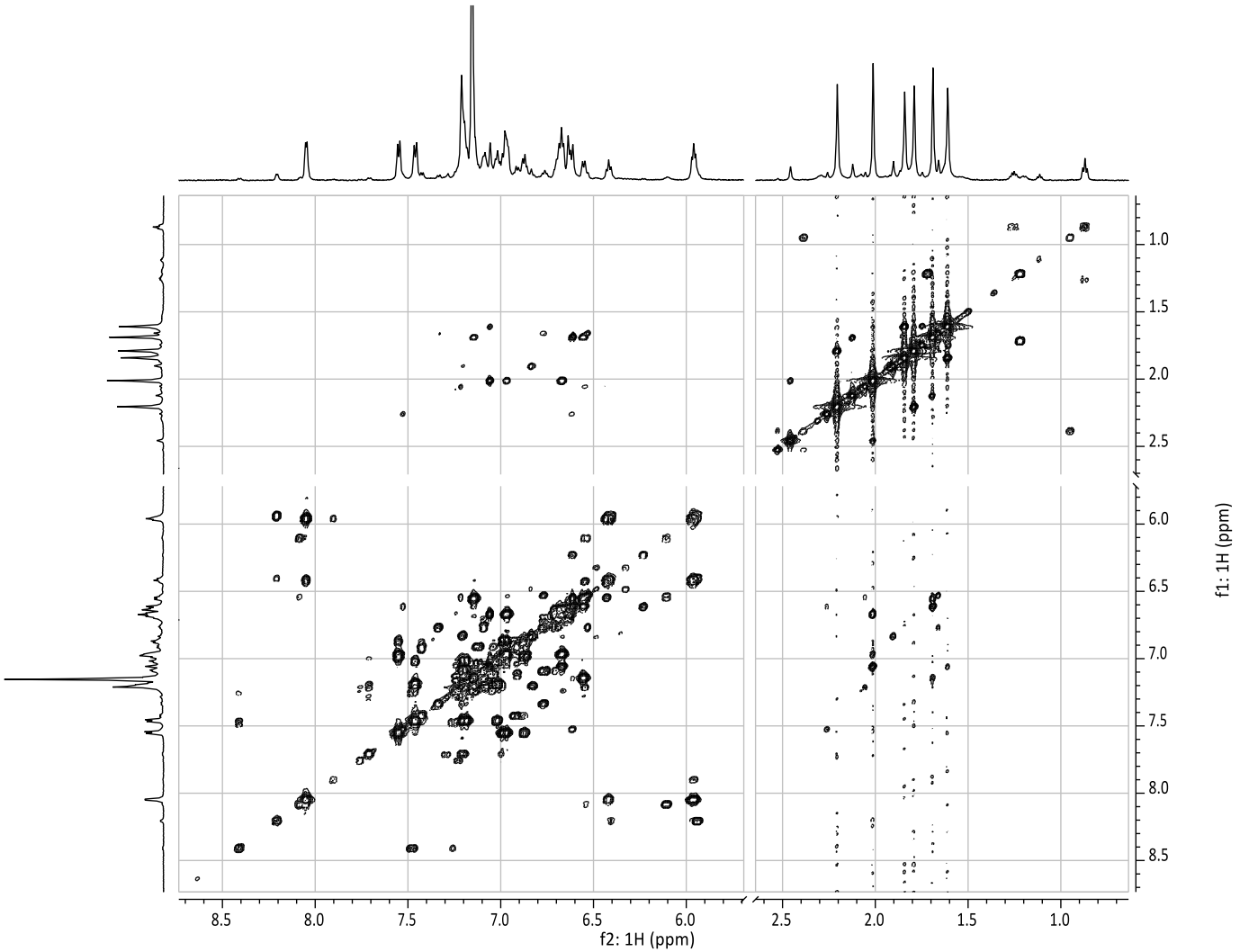


Figure 3.6 gCOSY spectrum of complex **3.1** in C_6D_6 at 25 °C. Empty segments cutout for clarity.

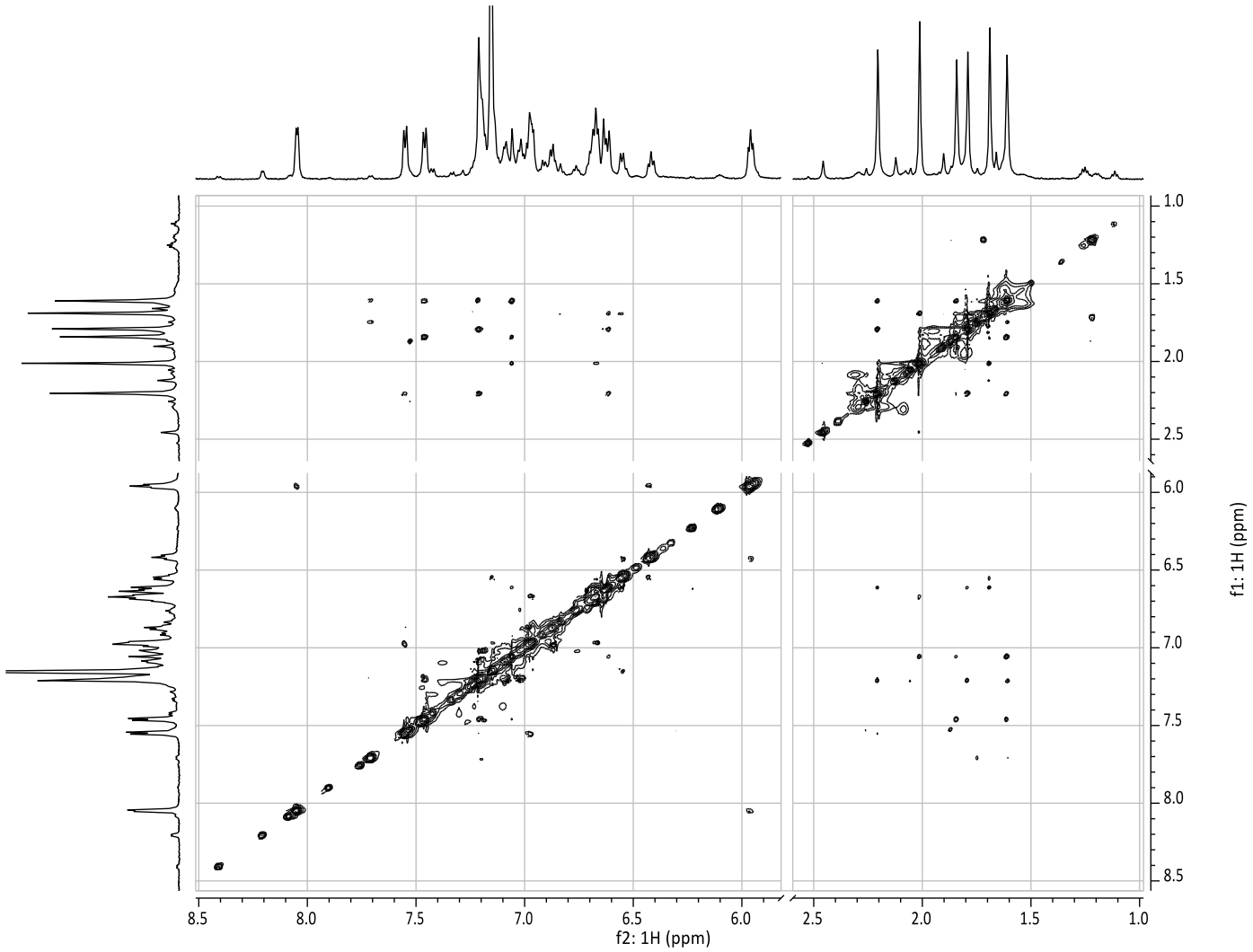


Figure 3.7 ROESYAD spectrum of complex **3.1** in C_6D_6 at 25 °C. Empty segments cutout for clarity.

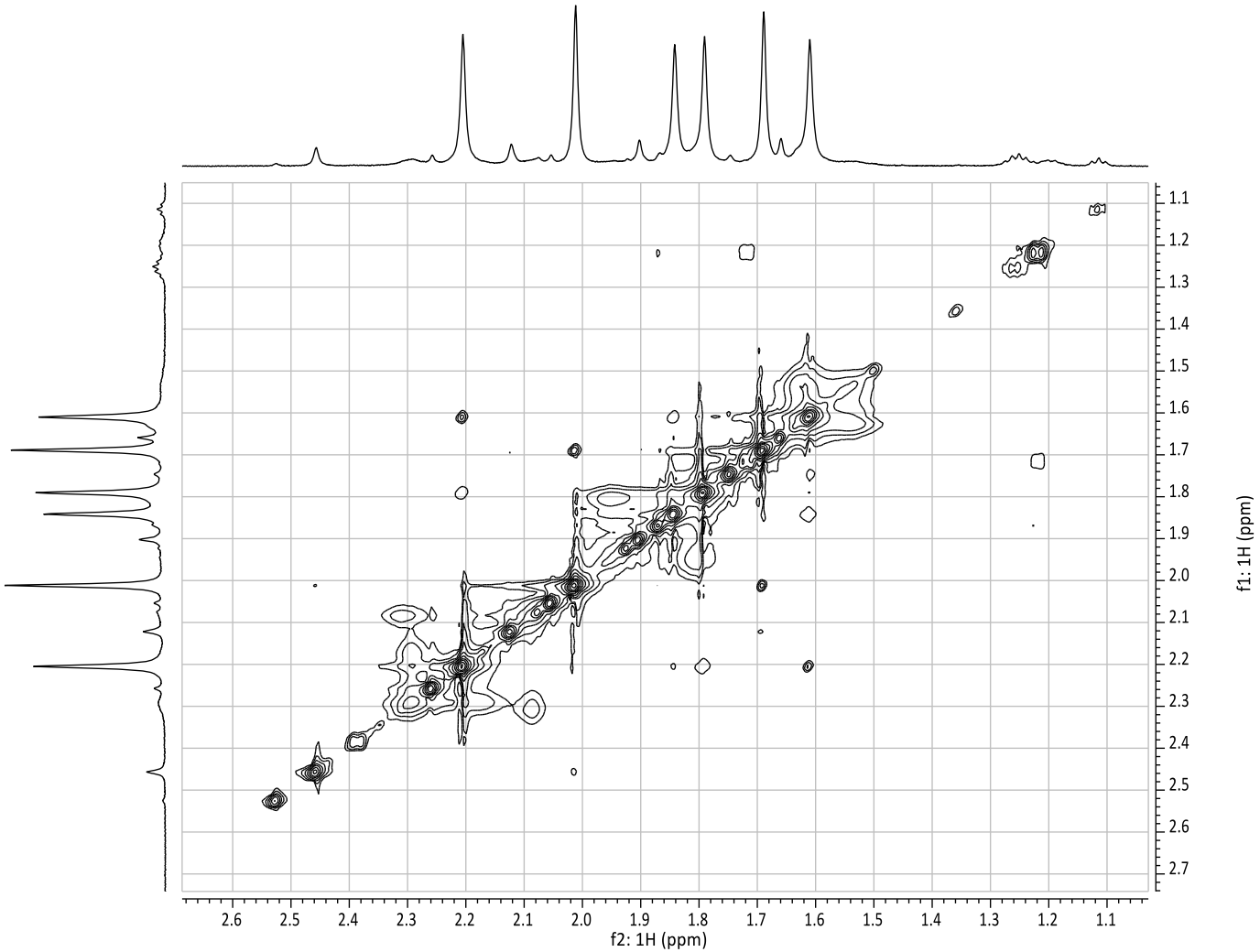


Figure 3.8 ROESYAD expansion of aliphatic region of complex **3.1** in C_6D_6 at 25 °C.

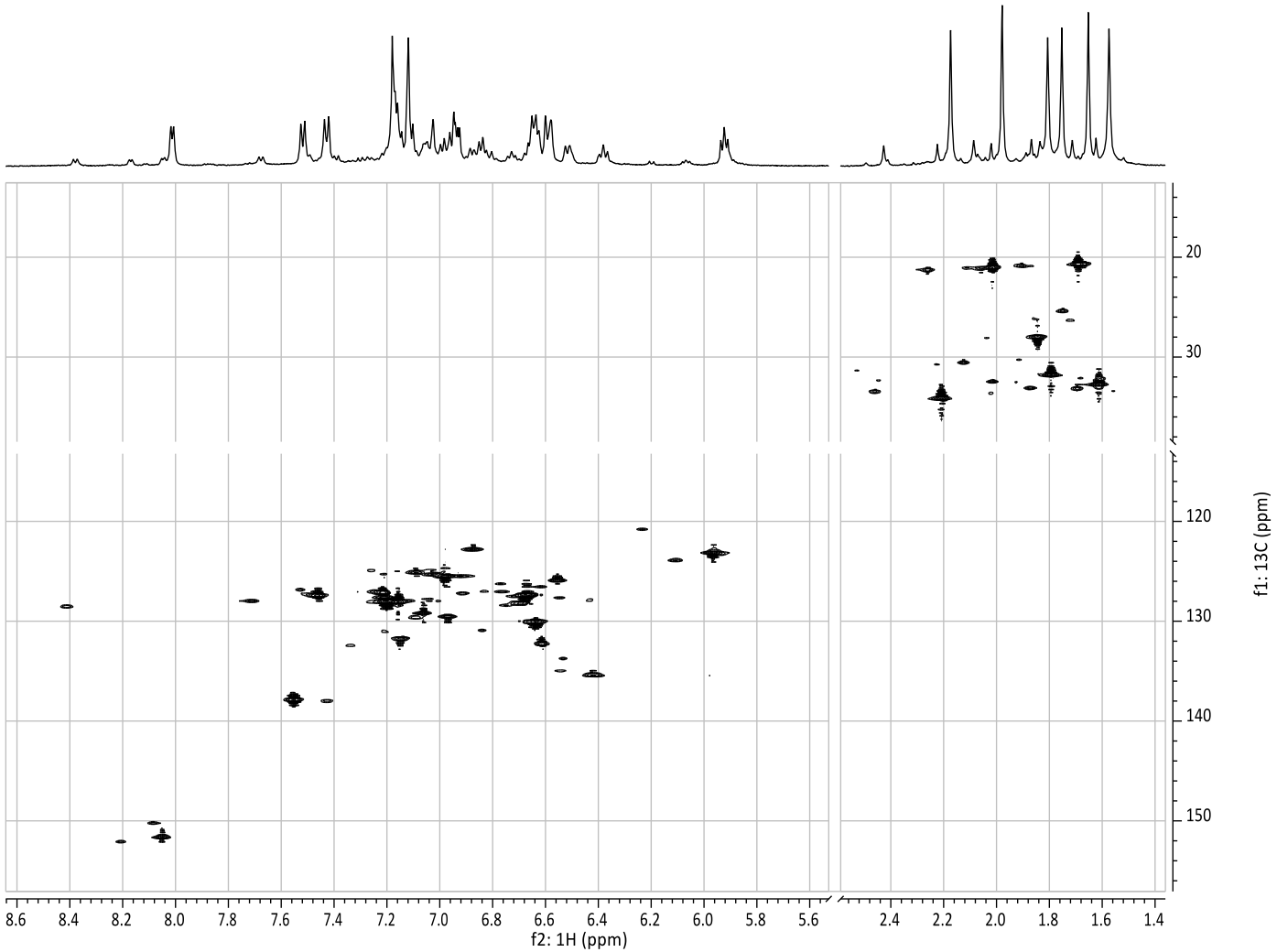


Figure 3.9 HSQCAD spectrum of complex **3.1** in C_6D_6 at 25 °C. Empty segments cutout for clarity.

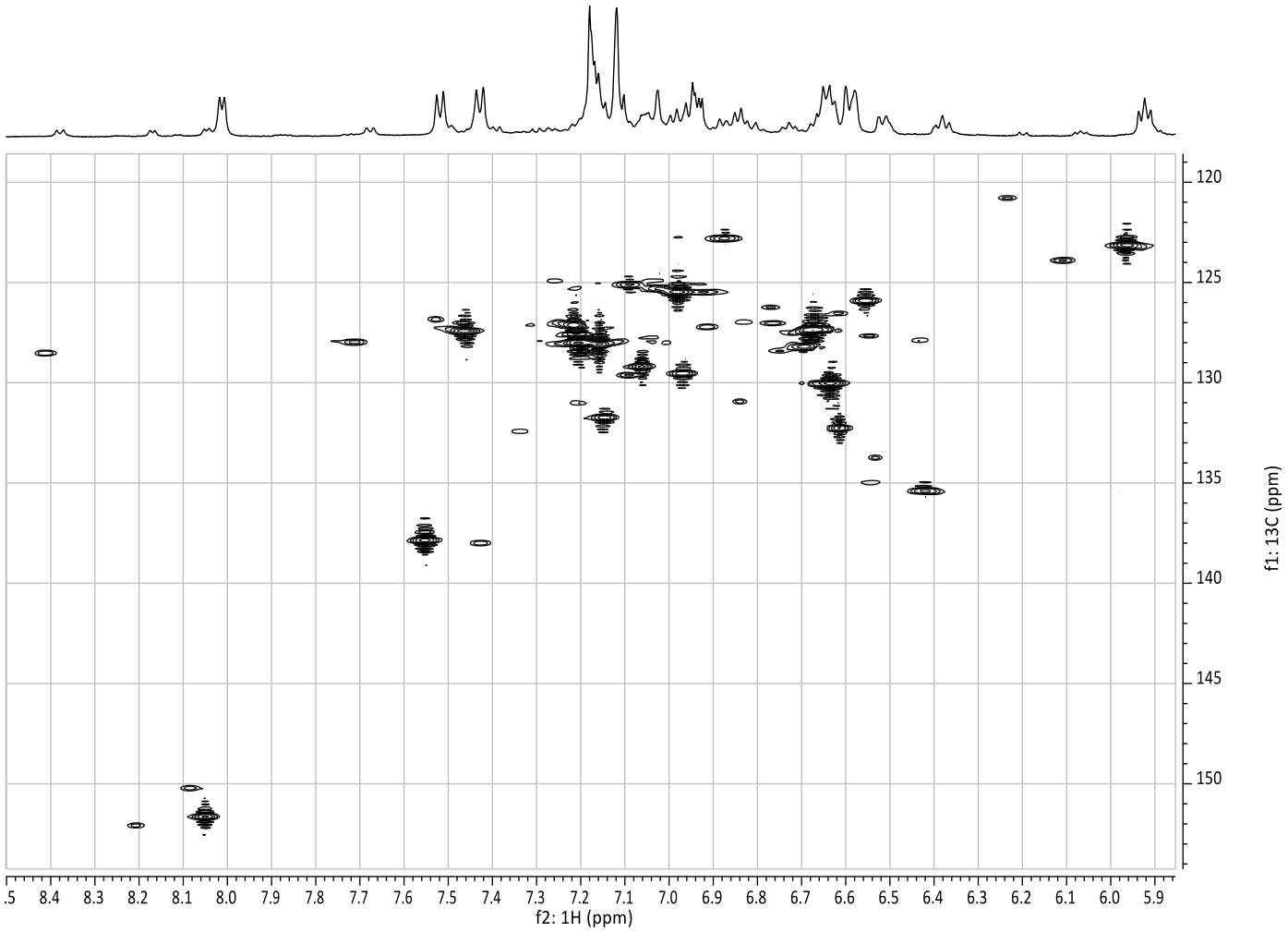


Figure 3.10 HSQCAD expansion of aromatic region of complex **3.1** in C_6D_6 at 25 °C.

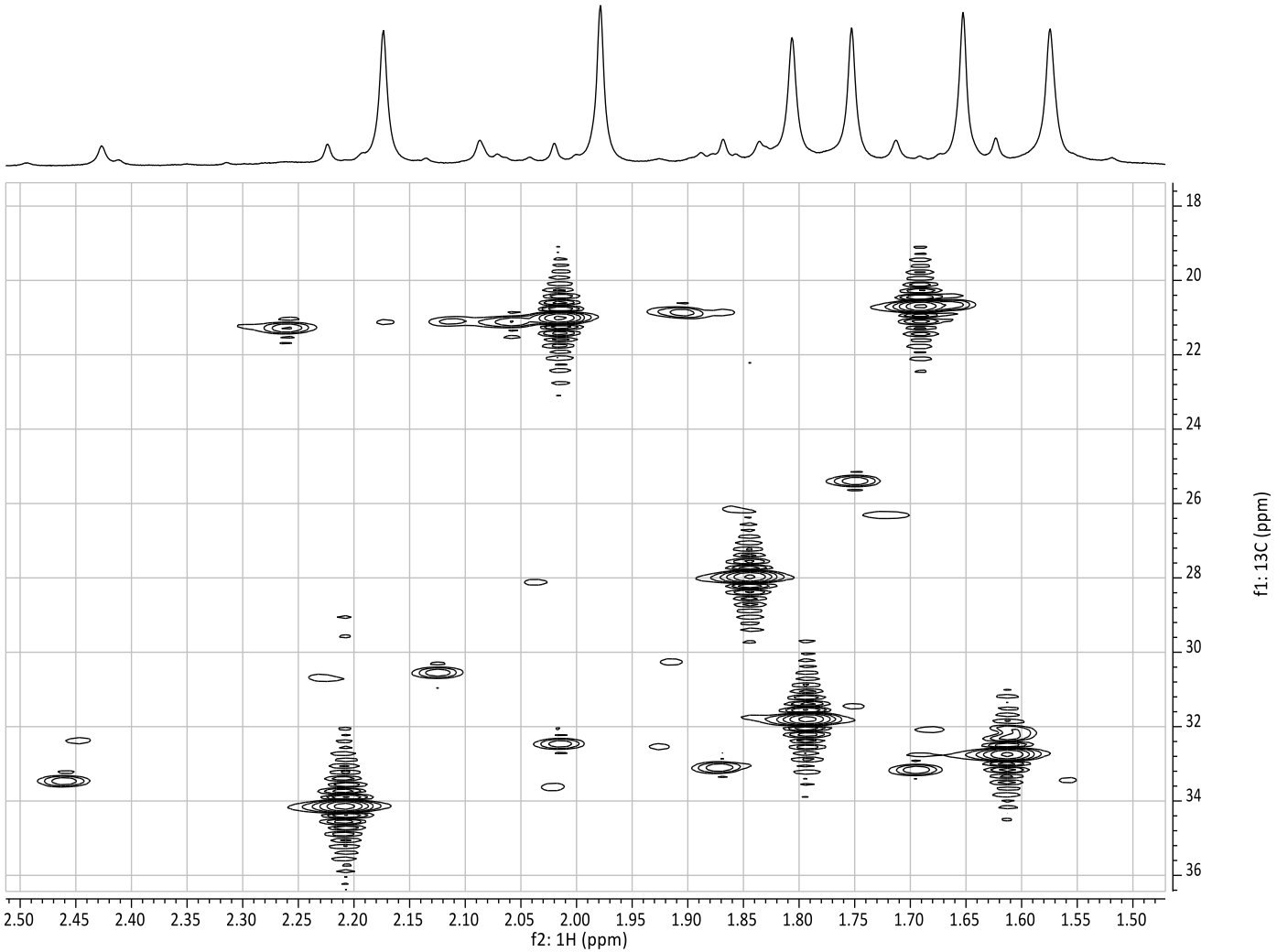


Figure 3.11 HSQCAD expansion of aliphatic region of complex **3.1** in C_6D_6 at 25 °C.

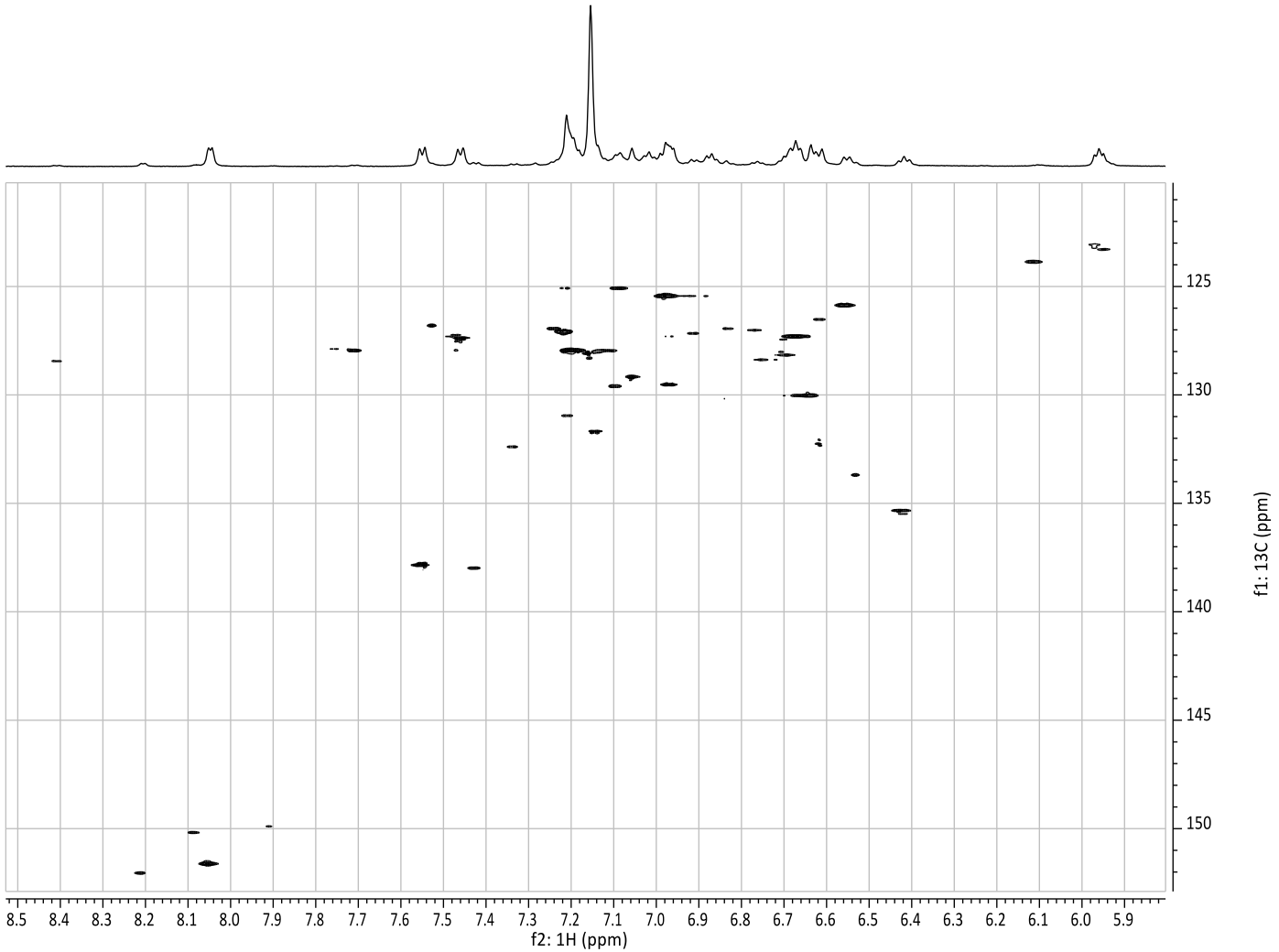


Figure 3.12 Band-selective HSQCAD spectrum of complex **3.1** in C_6D_6 at 25 °C.

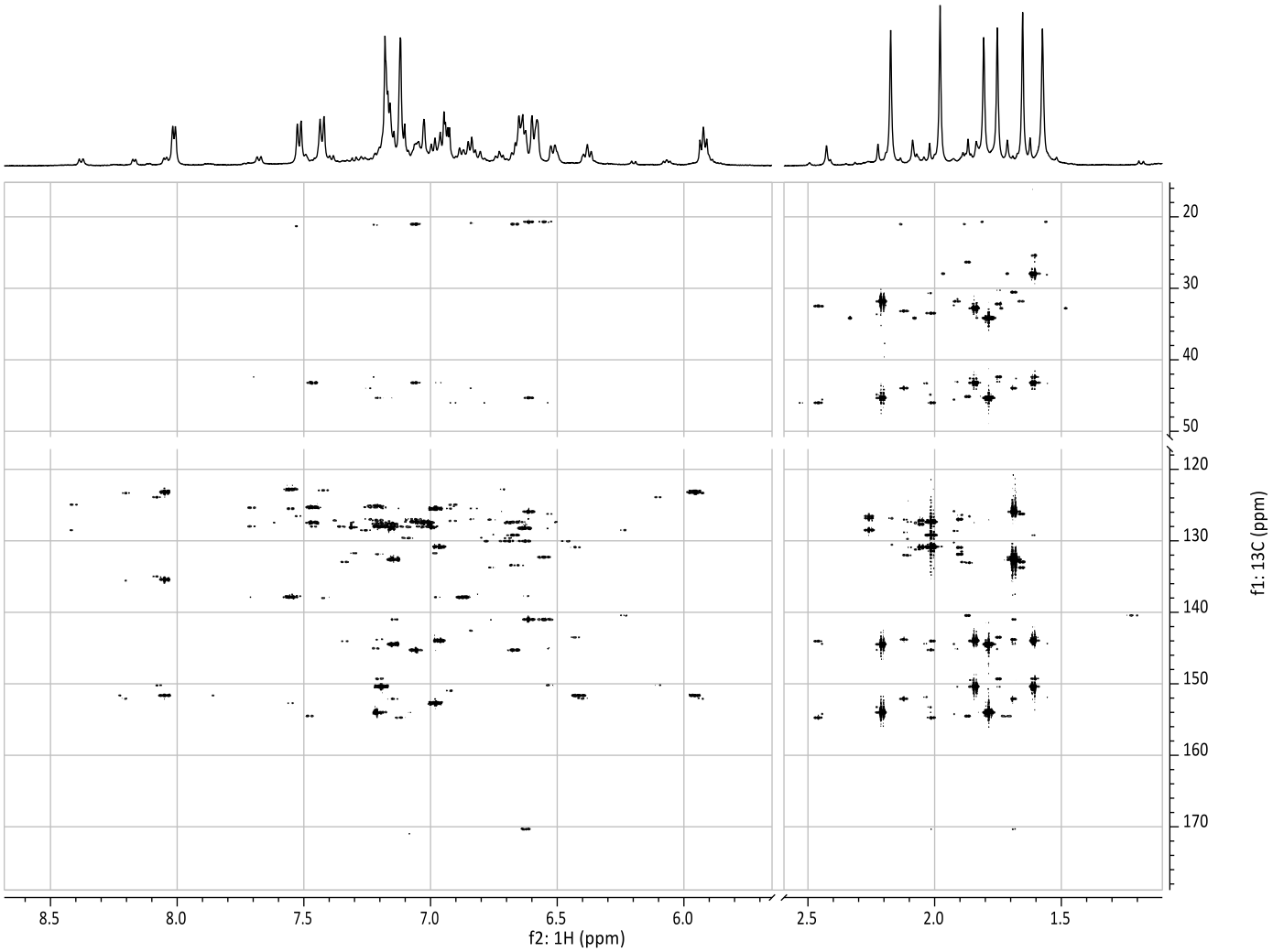


Figure 3.13 gHMBC spectrum of complex **3.1** in C_6D_6 at 25 °C. Empty segments cutout for clarity.

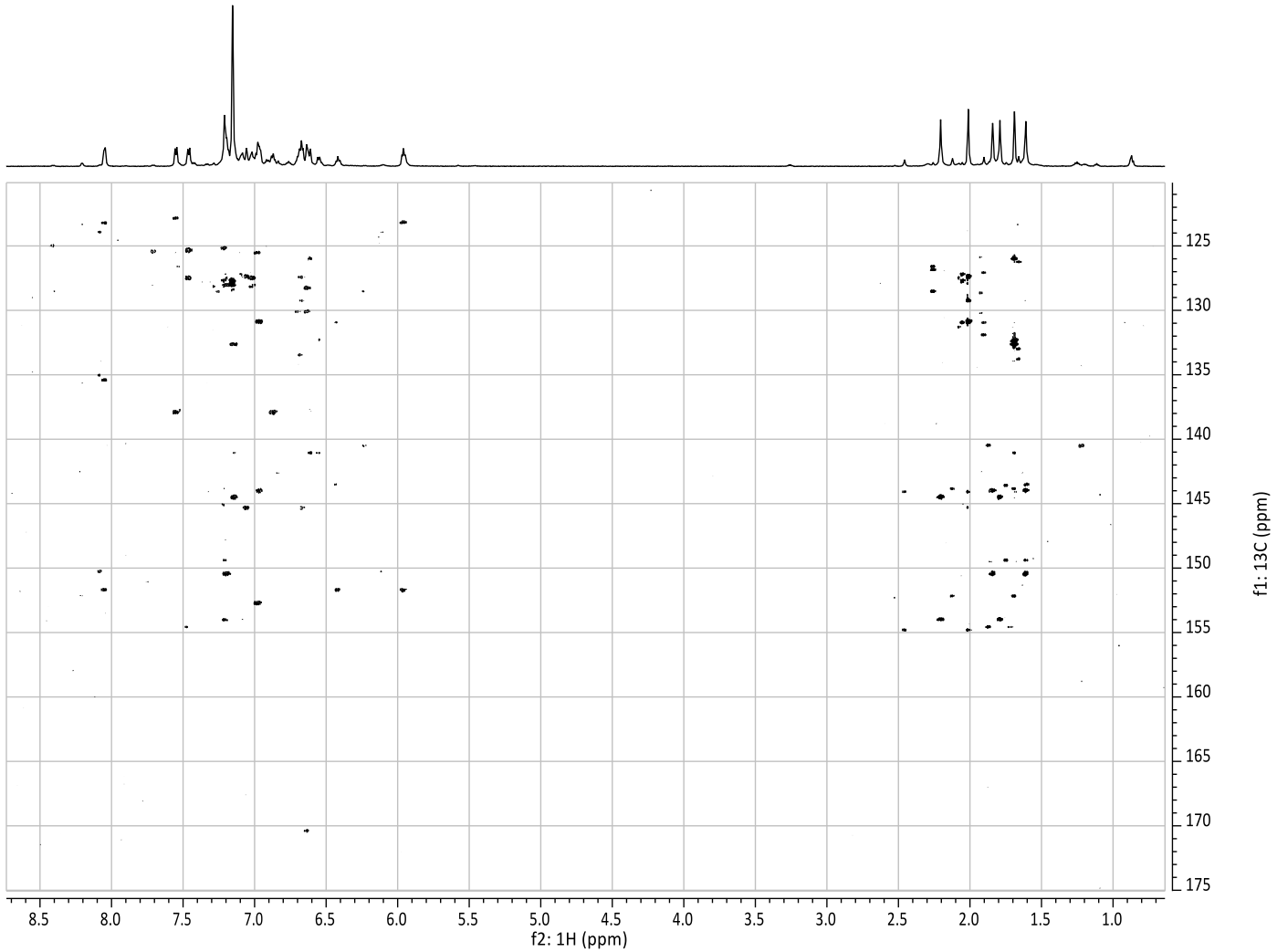
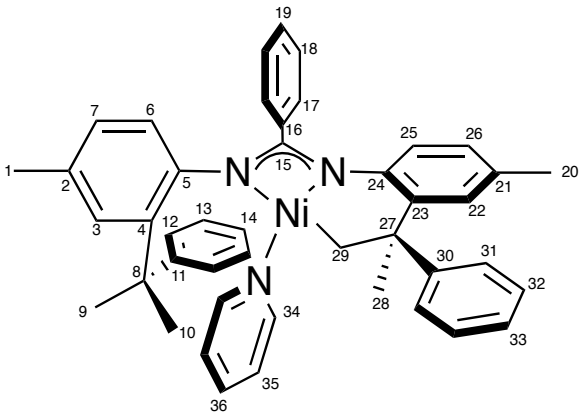


Figure 3.14 Band-selective gHMBC spectrum of complex **3.1** in C_6D_6 at 25 °C.

*3.4.2 Synthesis of **3.2***



Cyclometallation of catalyst 3.1 (3.2). Complex **3.1** (25 mg, 33 μmol) was taken up in minimal toluene layered with pentane at room temperature. Dark red crystals had formed after two days (20 mg, 89%). The ^{1}H and $^{13}C\{^{1}H\}$ NMR data obtained in C_6D_6 at room temperature are tabulated below. The resonances were assigned with the aid of COSY, HMBCAD, HSQCAD, and ROESY NMR experiments.

Table 3.5 NMR Data for complex **3.2**.

Carbon atom #	$^{13}C\{^{1}H\}$ NMR δ	^{1}H NMR δ	ROESY
1	21.08	2.06	
2	130.08	-	
3	127.15	7.22	C9
4	143.43	-	
5	144.99	-	
6	127.85	6.44	
7	127.63	6.55	
8	42.36	-	
9	32.14	1.61	C3, C12
10	25.38	1.75	C12, C34
11	149.27	-	
12	127.94	7.72	C9, C10
13	127.56	7.21	
14	125.34	7.00	
15			
16	130.95	-	
17	129.15	5.89 (b)	
18	127.51	6.21	
19	128.40	6.75	
20	21.08	2.06	
21	130.80	-	
22	126.81	7.22	
23	140.43	-	
24	137.66	-	
25	120.77	6.24	
26	126.52	6.63	
27	45.11	-	
28	33.07	1.87	
29	26.28	1.22 1.72	C31, C34
30	154.50	-	
31	128.49	8.42	C28, C29 (1.22)
32	127.28	7.48	
33	124.88	7.26	
34	150.19	8.09	C29 (1.22), C10
35	123.86	6.11	
36	134.95	6.57	

3.4.3 Ethylene Polymerization

General Procedure for Ethylene Polymerization at 0 °C (Table 1). In a glovebox, toluene, PMAO-IP, and/or the $Ni(COD)_2$ or copper cocatalyst was added to a 6 ounce (180 mL) round-bottom Laboratory Crest reaction vessel (Andrews Glass). The vessel was charged with an overpressure of ethylene and equilibrated at 0 °C for 10 min. Complex **3.1** was injected as a solution in 2 mL of dry, degassed toluene. The polymerization was quenched with methanol, the reaction mixture was precipitated into a copious amount of acidic methanol (2% HCl(aq)), and the resulting suspension was allowed to stir overnight. The polymer was isolated, rinsed with methanol, and dried to constant weight *in vacuo* at 60 °C.

3.4.4 X-Ray Data

Table 3.6 Crystal data and structure refinement for **3.1**.

Empirical formula	$C_{56}H_{55}N_3Ni$
Formula weight	828.74
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	Pna2(1)
Unit cell dimensions	a = 20.7648(8) Å α = 90°
	b = 12.2473(5) Å β = 90°
	c = 17.5693(7) Å γ = 90°
Volume	4468.1(3) $Å^3$
Z	4
Density (calculated)	1.232 Mg/m^3
Absorption coefficient	0.475 mm^{-1}
F(000)	1760
Crystal size	0.60 x 0.50 x 0.40 mm^3
Theta range for data collection	2.03 to 28.28°.
Index ranges	-27<=h<=22, -16<=k<=14, -23<=l<=23
Reflections collected	42752
Independent reflections	11089 [R(int) = 0.0381]
Completeness to theta = 28.28°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8327 and 0.7636
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11089 / 7 / 547
Goodness-of-fit on F^2	1.021
Final R indices [I>2sigma(I)]	R1 = 0.0364, wR2 = 0.0865
R indices (all data)	R1 = 0.0554, wR2 = 0.0966
Absolute structure parameter	-0.002(9)
Largest diff. peak and hole	0.346 and -0.268 $e.Å^{-3}$

Table 3.7 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^3$ x 10^3) for **3.1**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

atom	x	y	z	U(eq)
Ni(1)	7663(1)	6078(1)	5941(1)	20(1)
N(1)	7919(2)	7225(1)	7133(1)	22(1)
N(2)	8577(2)	5605(1)	7038(1)	20(1)
N(3)	7486(2)	4762(1)	4795(1)	21(1)
C(1)	7158(2)	8148(1)	7522(1)	20(1)
C(2)	6766(2)	8497(2)	8443(1)	24(1)
C(3)	5954(2)	9385(2)	8779(2)	30(1)
C(4)	5492(2)	9943(2)	8211(2)	31(1)
C(5)	5866(2)	9572(2)	7285(2)	27(1)
C(6)	6681(2)	8683(1)	6915(1)	21(1)
C(7)	7117(2)	8303(2)	5905(1)	22(1)
C(8)	8655(2)	8703(2)	5956(1)	23(1)
C(9)	9301(2)	8389(2)	5122(2)	30(1)
C(10)	10650(2)	8806(2)	5138(2)	35(1)
C(11)	11402(2)	9538(2)	5984(2)	38(1)
C(12)	10792(2)	9854(2)	6825(2)	36(1)
C(13)	9426(2)	9446(2)	6802(2)	29(1)
C(14)	6841(2)	7014(2)	5367(1)	23(1)
C(15)	6242(2)	8827(2)	5299(1)	29(1)
C(16)	4633(3)	10931(2)	8586(2)	52(1)
C(17)	9512(2)	4872(1)	7212(1)	19(1)
C(18)	10945(2)	5134(2)	7284(1)	24(1)
C(19)	11917(2)	4438(2)	7415(1)	25(1)
C(20)	11483(2)	3450(2)	7477(1)	24(1)
C(21)	10049(2)	3186(2)	7403(1)	22(1)
C(22)	9032(2)	3864(1)	7273(1)	19(1)
C(23)	7466(2)	3547(2)	7251(1)	22(1)
C(24)	6943(2)	4421(2)	8142(1)	24(1)
C(25)	5984(2)	5165(2)	8087(2)	29(1)

Table 3.7 (continued)

atom	x	y	z	U(eq)
C(26)	5535(2)	5936(2)	8906(2)	39(1)
C(27)	6033(3)	5979(2)	9796(2)	43(1)
C(28)	6980(3)	5244(2)	9874(2)	43(1)
C(29)	7434(2)	4475(2)	9055(2)	34(1)
C(30)	7197(2)	2390(2)	7287(2)	30(1)
C(31)	6630(2)	3465(2)	6308(1)	28(1)
C(32)	12529(2)	2678(2)	7609(2)	34(1)
C(33)	8483(2)	4030(2)	4657(1)	25(1)
C(34)	8370(2)	3019(2)	3885(2)	28(1)
C(35)	7169(2)	2703(2)	3230(2)	30(1)
C(36)	6145(2)	3436(2)	3359(1)	28(1)
C(37)	6343(2)	4451(2)	4133(1)	24(1)
C(38)	8647(2)	6683(2)	7597(1)	20(1)
C(39)	9486(2)	7275(2)	8558(1)	25(1)
C(40)	10298(2)	8256(2)	8731(2)	34(1)
C(41)	11075(3)	8845(2)	9620(2)	47(1)
C(42)	11010(3)	8472(2)	10350(2)	48(1)
C(43)	10195(3)	7510(2)	10185(2)	45(1)
C(44)	9443(2)	6902(2)	9281(2)	34(1)

Table 3.8 Crystal data and structure refinement for **3.2**.

Empirical formula	$C_{44}H_{44}N_3Ni$
Formula weight	673.53
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 9.6499(7) Å α = 12.977(3)°
	b = 13.0686(9) Å β = 5.925(3)°
	c = 15.2694(11) Å γ = 2.195(3)°
Volume	1756.9(2) $Å^3$
Z	2
Density (calculated)	1.271 Mg/m^3
Absorption coefficient	0.588 mm^{-1}
F(000)	712
Crystal size	0.15 x 0.05 x 0.02 mm^3
Theta range for data collection	2.13 to 28.28°.
Index ranges	-10<=h<=12, -17<=k<=17, -20<=l<=20
Reflections collected	33905
Independent reflections	8561 [R(int) = 0.0479]
Completeness to theta = 28.28°	99.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9883 and 0.9170
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8651 / 0 / 549
Goodness-of-fit on F^2	0.994
Final R indices [I>2sigma(I)]	R1 = 0.0398, wR2 = 0.0806
R indices (all data)	R1 = 0.0634, wR2 = 0.0908
Largest diff. peak and hole	0.290 and -0.445 $e.Å^{-3}$

Table 3.9 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^3$ x 10^3) for **3.2**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

atom	x	y	z	U(eq)
Ni(1)	8675(1)	6068(1)	12578(1)	30(1)
N(1)	8249(1)	4676(1)	12203(1)	30(1)
N(2)	9245(1)	4872(1)	12551(1)	30(1)
N(3)	7975(1)	7044(1)	12593(1)	38(1)
C(1)	7608(1)	4313(2)	12352(1)	30(1)
C(2)	7448(1)	3989(2)	13087(1)	37(1)
C(3)	6819(1)	3767(2)	13300(1)	44(1)
C(4)	6327(1)	3863(2)	12777(1)	41(1)
C(5)	6490(1)	4159(2)	12042(2)	38(1)
C(6)	7120(1)	4383(2)	11804(1)	33(1)
C(7)	7255(1)	4649(2)	10959(1)	37(1)
C(8)	7642(1)	3704(2)	10610(1)	35(1)
C(9)	7422(1)	2632(2)	10702(1)	45(1)
C(10)	7747(2)	1769(2)	10375(2)	54(1)
C(11)	8295(1)	1936(2)	9952(2)	58(1)
C(12)	8515(1)	2992(3)	9856(2)	55(1)
C(13)	8188(1)	3864(2)	10179(1)	42(1)
C(14)	7585(1)	5764(2)	10881(1)	43(1)
C(15)	6631(1)	4729(3)	10481(2)	54(1)
C(16)	5636(1)	3614(2)	12985(2)	52(1)
C(17)	9903(1)	4644(2)	12713(1)	28(1)
C(18)	10104(1)	4777(2)	13466(1)	35(1)
C(19)	10728(1)	4598(2)	13681(1)	35(1)
C(20)	11184(1)	4269(2)	13163(1)	33(1)
C(21)	10987(1)	4164(2)	12411(1)	31(1)
C(22)	10356(1)	4370(2)	12163(1)	28(1)
C(23)	10243(1)	4256(2)	11297(1)	33(1)
C(24)	10766(1)	4902(2)	10873(1)	34(1)

Table 3.9 (continued)

atom	x	y	z	U(eq)
C(25)	11096(1)	4484(2)	10257(1)	51(1)
C(26)	11525(2)	5129(3)	9848(2)	64(1)
C(27)	11633(1)	6179(3)	10045(2)	57(1)
C(28)	11303(1)	6619(3)	10653(2)	58(1)
C(29)	10873(1)	5984(2)	11062(2)	49(1)
C(30)	10260(1)	3028(2)	11107(1)	48(1)
C(31)	9600(1)	4717(2)	10996(1)	45(1)
C(32)	11876(1)	4072(2)	13390(1)	42(1)
C(33)	9242(1)	7130(2)	12962(1)	37(1)
C(34)	9739(1)	7529(2)	12520(2)	58(1)
C(35)	10181(1)	8295(3)	12804(2)	75(1)
C(36)	10125(2)	8654(2)	13543(2)	65(1)
C(37)	9621(2)	8299(2)	13982(2)	67(1)
C(38)	9177(2)	7560(2)	13690(2)	55(1)
C(39)	8773(1)	4164(2)	12471(1)	29(1)
C(40)	8815(1)	2969(2)	12624(1)	29(1)
C(41)	8612(1)	2240(2)	12078(1)	40(1)
C(42)	8621(1)	1126(2)	12218(2)	49(1)
C(43)	8828(1)	737(2)	12917(2)	47(1)
C(44)	9025(1)	1465(2)	13463(1)	44(1)
C(45)	9029(1)	2579(2)	13318(1)	37(1)
C(46)	7972(1)	7978(2)	12207(2)	51(1)
C(47)	7427(2)	8636(2)	12164(2)	72(1)
C(48)	6881(2)	8330(2)	12540(3)	72(1)
C(49)	6883(1)	7387(3)	12961(2)	60(1)
C(50)	7433(1)	6769(2)	12976(2)	46(1)
C(1S)	10343(2)	2211(4)	15145(2)	87(1)
C(2S)	10146(2)	1164(5)	15357(3)	123(2)
C(3S)	10661(3)	438(4)	15600(3)	114(2)
C(4S)	11247(2)	759(3)	15617(3)	85(1)
C(5S)	11389(2)	1721(3)	15405(2)	82(1)
C(6S)	10968(2)	2438(3)	15178(2)	80(1)

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